

Chapter 8

Quality Assurance of Ambient Air Toxic Organic Compounds Monitoring

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Table of Contents

	Page
1.0 General Project Description.....	1
1.1 Objective and Scope	1
1.2 Urban Air Toxics Monitoring Program	1
1.3 Photochemical Assessment Monitoring Program	2
1.4 Carbonyl Monitoring Program.....	3
1.5 Data Utilization.....	3
1.6 Quality Assurance Objectives.....	3
2.0 Responsible Parties	3
3.0 Urban Air Toxics Monitoring Program.....	4
3.1 Site Selection	4
3.2 Sampling Procedures	4
3.2.1 Air Canister Sampling Equipment for Air Toxics	4
3.2.2 Air Canister Sampling Procedures.....	4
3.2.3 Grab Sampling for Citizen Complaints.....	5
3.3 Chain-of-Custody.....	6
3.3.1 Air Toxics Canister Sample Documentation	6
3.3.2 Air Toxics Canister Chain-of-Custody Tag.....	7
3.4 Analytical Equipment	7
3.5 Calibration Procedures and Frequency	7
3.6 Data Reduction.....	8
3.7 Data Validation	9
3.8 Quality control and Quality Assurance.....	9
3.8.1 Air Canister Sampling Quality Control/Quality Assurance.....	9
3.8.2 Analysis Quality Control/Quality Assurance.....	10
3.9 Data Precision and Accuracy	11
3.9.1 Entire System Precision	11
3.9.2 Entire System Accuracy.....	11
3.9.3 VOC Analysis Accuracy.....	12
3.9.4 VOC Canister Sampling Precision.....	12
3.9.5 VOC Canister Sampling Accuracy	12
3.9.6 Reporting Agency Accuracy and Precision	12
3.10 System Audits	12
3.11 Corrective Action.....	13
3.11.1 SUMMA Canisters.....	13
3.11.2 GC/MS Analysis	13

4.0	Photochemical Assessment Monitoring Program (PAMS)	13
4.1	Site Selection	14
4.2	Sampling Procedures	14
4.2.1	Remote Sampling	14
4.2.2	Canister Sampling	14
4.3	Chain-of-Custody	14
4.3.1	Canister Sample Documentation	14
4.3.2	Remote Analysis Documentation	14
4.4	Analytical Equipment	15
4.5	Calibration Procedures and Frequency	15
4.6	Data Reduction	15
4.7	Data Validation	16
4.8	Quality Control and Quality Assurance	16
4.9	Data Precision and Accuracy	16
4.10	System Audits	17
5.0	Carbonyl Monitoring Program	17
5.1	Site Selection	17
5.2	Sampling Procedures	17
5.3	Chain-of-Custody	18
5.4	Analytical Procedures	18
5.5	Data Validation	18
5.6	Analysis Quality Control/Quality Assurance	19
5.6.1	Analysis Precision	19
5.6.2	Analysis Accuracy	19
5.7	Sampling Quality Control/Quality Assurance	19
5.8	Corrective Action	20
5.8.1	Carbonyl Sampling Cartridges	20
6.0	Lead Analysis Program	20
6.1	Analysis Quality Control & Quality Assurance	20
6.1.1	Lead Strip Analysis	20
6.1.2	Collocated Monitoring	21

APPENDICES

A	Air Toxics Siting Criteria	21
B	Procedure for Cleaning Canisters	23
C	Procedure for TNMOC Determination	25
D	Procedure for Grab Sampling	31
E	Procedure for Canister Chain-of-Custody and Sample Logging	32
F	Procedure for GC/MS Analysis of TO Compounds and Ozone Precursors	33
G	Select Air Toxics Procedures and Guidelines	45
H	Procedure for Carbonyl Monitoring and Handling DNPH Cartridges	51
I	Procedure for Meriter Sampler Canister Pick-Up and Set-Up	52

REFERENCES

Attachment #1 (Canister Chain-of-Custody Tag)	56
Attachment #2 (Monitored TO-15 VOC's)	57
Attachment #3 (Ozone Precursors)	58
Attachment #4 (Carbonyl Cartridge Chain-of-Custody Tag)	59

QA Manual Abbreviations & Acronyms

Below are common abbreviations used in this manual. Explanations for additional abbreviations of limited use will be found in the section where used.

AIRS	Aerometric Information and Retrieval System
amu	Atomic mass unit
ASTM	American Society for Testing Materials
atm	Atmospheric Pressure
AQS	Air Quality System
CAAP	Continuous Aerometric Acquisition Program. In IDEM, CAAP almost always means monitoring station
CAMS	Continuous Air Monitoring Station
°C	Degrees Celsius (centigrade)
cc	Cubic Centimeter. It is the same as a milliliter (see ml).
CFR	Code of Federal Regulations
CO	Carbon Monoxide
CO ₂	Carbon Dioxide
CRM	Certified Reference Material
DNPH	Dinitro Phenyl Hydrazine (comes in a cartridge for carbonyl monitoring)
°F	Degrees Fahrenheit
FID	Flame Ionization Detector (seen commonly in conjunction with "GC")
Free Radical	An atom or molecule that bears an unpaired electron and is extremely reactive, capable of engaging in rapid chain reactions that destabilize other molecules
GC	Gas Chromatograph
GC/MS	GC combined with a Mass Spectrometer instead of FID
HAP	Hazardous Air Pollutant
Hg	Mercury
HPLC	High Performance Liquid Chromatography
hr	Hour
IDEM	Indiana Department of Environmental Management
K	Kelvin (273 + temperature °C)
l	Liter
LEADS	Leading Environmental Analysis and Display System
m	Meter
MCPC	Measurement Principle and Calibration Procedure
min	Minute
ml	Milliliter
mm	Millimeter
mmHg	Millimeters of Mercury
MS	Mass Spectrometer
NAAQS	National Ambient Air Quality Standards
NAMS	National Air Monitoring Stations
NESHAP	National Emissions Standards for Hazardous Air Pollutants
ng	Nanograms
NIST	National Institute of Standards and Technology

nm	Nanometers
NMOC	Non-Methane Organic Compounds
NO	Nitric Oxide
NO ₂	Nitrogen Dioxide
NO _x	Nitrogen Oxides
NO _y	NO _x + HNO ₃ + organic nitrates + inorganic nitrates
NPAAQS	National Primary Ambient Air Quality Standards
NPAP	National Performance Audit Program
NSAAQS	National Secondary Ambient Air Quality Standards
OAQ	Office of Air Quality
P&A	Precision and Accuracy
PAMS	Photochemical Assessment Monitoring Station
PAMHC	Photochemical Assessment Monitoring Hydrocarbons
Pb	Lead
PM ₁₀	Particulate Matter (less than 10 microns)
ppb	Parts per Billion
ppbC	Parts per Billion of Carbon
ppbv	Parts per Billion by Volume
ppmC	Parts per Million of Carbon
PSD	Prevention of Significant Deterioration
psia	Pounds per square inch absolute
psig	Pounds per square inch gauge
QA	Quality Assurance (External)
QC	Quality Control (Internal)
RMD	Reference Method for the Determination
SIP	State Implementation Plan
SLAMS	State and Local Air Monitoring Stations
SO ₂	Sulfur Dioxide
SRC	Standard Reference Conditions (760 mmHg & 298 Kelvin)
torr	Pressure unit equivalent to mmHg
SRM	Standard Reference Materials
TNMOC	Total Non-Methane Organic Compounds
TO	Toxic Organics
TO-15	EPA Compendium Method for the determination of toxic organic compounds in air. IDEM monitors for 62 specific compounds using this method (see Attachment #2)
TSP	Total Suspended Particulates
µg	Microgram
µl	Microliter
USEPA	U.S. Environmental Protection Agency
UTM	Universal Transverse Mercator
UV	Ultraviolet
VDR	Valid Data Return
VOC	Volatile Organic Compound. This is a general term used in the chapter encompassing toxic organics, NMOC and ozone precursor compounds

1.0 General Project Description

1.1 Objective and Scope

The objective of the State of Indiana's air toxic monitoring program is to determine background ambient concentrations of selected hazardous air pollutants listed in the Clean Air Act of 1990. The monitoring data will be used for evaluating population exposure and risk assessment. The data will also be used for planning for compliance with standards that are being developed by the USEPA. Additional applications encompass episode monitoring (i.e. chemical spills and fires), hazardous waste site monitoring, nuisance complaints, and source specific ambient monitoring.

The scope of the air toxic monitoring program includes taking representative ambient air samples for the analysis of volatile organic compounds. The various types of air toxics monitoring are described below:

1. VOC is an acronym entailing all volatile organic compounds from methane to halogenated compounds.
2. Total NMOC (non-methane organic carbon) is used to determine the concentration of organic compounds present in the sample excluding methane. This information is used to determine the amount of volume to be trapped in a subsequent analysis on a GC/MS system which is very sensitive to higher concentrations of VOC's.
3. TO-15 compounds list consist of sixty-two VOC's classified by the EPA as hazardous air pollutants. This includes polar and non-polar organic compounds such as ethanol, isopropyl alcohol, and benzene. (see Attachment #2)
4. Photochemical Assessment Monitoring (PAMS) hydrocarbons are a group of hydrocarbon compounds which are responsible for ozone formation in atmosphere. They are also referred as ozone precursor compounds. They are monitored under the PAMS (Photochemical Assessment Monitoring Station) program. The other species monitored under the PAMS program includes carbonyl compounds, nitrous oxide, and NO_y. (see Attachment #3)
5. Carbonyl monitoring also falls under the PAMS monitoring program. Carbonyl compounds are monitored using USEPA method TO-11. The monitoring compound list consists of formaldehyde, acetaldehyde, and acetone. Atmospheric carbonyls, unlike PAMS, not only cause high ozone levels, but are also a result of high ozone levels.
6. High volume total suspended particulate (TSP) samples for selected metals are discussed in Section 6.0 of this chapter

1.2 Urban Air Toxics Monitoring Program

The first urban air toxics site in Indiana was established in 1988 and since then the number of sites has been increased to nine. The toxic compounds are monitored in ambient air using

USEPA approved methodology for sampling and analysis (see Reference 15). Samples are collected using a stainless steel SUMMA canister. The inner surface of the canisters is electro polished to eliminate the active sites to maintain the integrity of the sample. Samples of ambient air are collected every six days for 24 hours. The samples are then analyzed for TNMOC (total non-methane organic compounds) using an USEPA Method TO-12 followed by a GC/MS analysis using USEPA method TO-15 for sixty HAP's. The instrumentation and analysis procedure is described in the Air Toxic Section's SOPs (see SOP <https://extranet.idem.in.gov/standards/docs/sops/oaq/S-005-OAQ-M-AT-11-T-R1.pdf> and <https://extranet.idem.in.gov/standards/docs/sops/oaq/S-009-OAQ-M-AT-11-T-R1.pdf>)

Current monitoring locations are as follows:

Clarksville	
East Chicago	Indianapolis-Washington Park
Gary IITRI	Ogden Dunes
Hammond	Terre Haute
Whiting High School	University of Evansville

All monitoring data and site information are posted on IDEM's Toxics Data page (<http://www.in.gov/idem/toxic/2362.htm>). The purpose of this sampling is to assess possible NESHAP violations under Title III. The Toxics Data web site is available to all interested parties including the USEPA and other state and local agencies.

1.3 Photochemical Assessment Monitoring Program (PAMS)

This is an USEPA mandated program initiated to provide an air quality database to assist in refining air pollution control strategies for attaining the ozone NAAQS. The PAMS program began in 1994 in order to study the chemical species involved in atmospheric ozone formation. The PAMS program requires the establishment of an enhanced monitoring network in all ozone non-attainment areas classified as serious, severe, or extreme.

PAMS compounds (ozone precursors), as mandated under Title I of the Clean Air Act, are monitored continuously on an hourly basis at the remote site located in Gary, Indiana. Continuous monitoring at the Gary site is required to be performed from June 1st to August 31st. Indiana began year-round monitoring of ozone precursor compounds at the Gary site in March 2012. Indiana also began year-round monitoring of ozone precursor compounds at the Indianapolis Washington Park site in August of 2011. Another requirement of the PAMS monitoring program is to collect a 24 canister sample every six days throughout the year. Canister samples are also analyzed for fifty-six ozone precursor compounds as well as TO-15 compounds.

The Gary, Indiana PAMS site is classified as a Type 2 site. The Type 2 sites are designated as maximum ozone precursor emissions impact sites. Type 2 sites are designed to collect data on the type and magnitude of ozone precursors.

1.4 Carbonyl Monitoring Program

Another requirement of a PAMS Type 2 site is to monitor and collect data on three specific carbonyl compounds (formaldehyde, acetaldehyde, and acetone) every three hours during the ozone monitoring season. The monitoring of carbonyl containing compounds in the atmosphere is of interest because of their importance as precursors in the production of photochemical smog and as a major source of free radicals in the atmosphere.

1.5 Data Utilization

Air quality data obtained from this program is intended to be used by the State of Indiana, Local Agencies and the Lake Michigan Air Directors Consortium (LADCO) to:

- provide a basis to determine risk levels and identify the need for further detailed assessment in the areas under study;
- coordinate a State Implementation Plan (SIP) for reduction of ozone associated with air toxics;
- perform screening, risk exposure assessment, and modeling analysis; and
- develop/implement air quality regulations.

1.6 Quality Assurance Objectives

The objectives of the State of Indiana air toxic quality assurance activities are to define and report precision, accuracy, completeness, representativeness, and comparability of the data generated from air toxics analysis.

2.0 Responsible Parties

PROJECT MANAGEMENT

Office of Air Quality Assistant Commissioner
Air Monitoring Branch Chief

SAMPLING

Ambient Monitoring Section Chiefs

AIR TOXICS ANALYSIS

Air Toxics Section Chief

QUALITY ASSURANCE

Quality Assurance Section Chief

DATA VALIDATION

Quality Assurance Section Chief
Ambient Monitoring Section Chiefs
Air Toxics Section Chief

3.0 Urban Air Toxics Monitoring Program

3.1 Site Selection

Monitoring sites are located to represent the average ambient air quality of the area. The following criteria are used to determine site selection (see References 6, 7, and 14):

- High population density
- Multiple source, multiple pollutant area, not unduly dominated by one source
- Area of typical urban exposure
- Meets criteria found in the literature
- General guidelines for siting criteria (see Appendix A)

3.2 Sampling Procedures

3.2.1 Air Canister Sampling Equipment for Air Toxics

The following equipment is utilized for obtaining a representative 24-hour air sample for analysis:

- Meriter Sampler: an automatic, programmable canister sampler installed at each monitoring site. Each sampler is certified prior to being put into the field for sampling.
- 6L SUMMA canisters: spherical, stainless steel canisters which have had their inner surface electro polished to remove surface active sites. Electro polishing ensures the stability of the canister samples up to three months.

3.2.2 Air Canister Sampling Procedures (see Appendix I)

1. Sample canister should be installed with enough time to detect any possible leak prior to sampling period.
2. Obtain a 6L SUMMA canister that has been certified to be free of contamination and has been evacuated to approximately -29 inches of mercury. Any canister with a pressure higher than -25 inches of mercury must not be used.
3. Verify that the timer, pumps, and solenoid valve are operating properly.

4. Verify that the flow controller is correctly calibrated and set to 6.5 cc/min for a 24-hour sample time. The flow controller must be able to produce a flow in the range of 5.5 to 8 cc/min.
5. Verify that the timer is certified, calibrated, and correctly set for the desired sample period and that the solenoid valve is closed.
6. Connect the certified SUMMA canister to the solenoid valve.
7. Open the canister valve and record its initial pressure reading on the absolute gauge.
8. Set the clock(s) for the desired sample period.
9. After the sample period, record the final pressure reading in psig and close the canister valve.
10. Fill out the canister's identification tag as necessary. Return canister to laboratory within 14 days for analysis.
11. Complete records of the sampling should be entered in a bound notebook located at the site, including meteorological conditions or unusual events that may affect sample composition.

3.2.3 Grab Sampling for Citizen Complaints

Grab samples of ambient or indoor air are collected in air sampling canisters using a sample probe (see Appendix D). The sample probe is made using 1/4" stainless steel tubing which is attached to a flow metering valve and a seven micron particulate filter which is capped with a 1/4" plug. The sample flows through the particle filter and is regulated by the flow metering valve, after which it enters the canister.

1. Obtain a 6L SUMMA canister with a plug that has been certified to be free of contamination and has been evacuated to approximately -29 inches of mercury. Any canisters not evacuated in a -25 to -30 inches of mercury must not be used. (See [Toxic Sampler Setup and Pickup Lab Commerce - Meriter MCS-1-R](#))
2. Remove canister plug and attach the sample probe to the canister inlet. Tighten the nut to finger-tight, then turn an additional 1/4 turn with a wrench.
3. Verify that the flow metering valve on the sample probe is in the off position.
4. Open the canister valve. If you hear air entering the canister at this time, close the canister valve and re-check the flow metering valve and the canister's inlet connection to ensure that both are closed or turned off.

5. Open the flow metering valve and set the flow directly between 0 and 1 on the meter scale. This corresponds to a sample flow of 150 ml/minute.
6. Monitor the flow metering valve so that it's always between 0 and 1. Flow rate will continue to drop until the canister has reached atmospheric pressure. At this point, flow can no longer be adjusted.
7. Close the canister valve and the flow metering valve.
8. Remove the probe from the canister.
9. To ensure that the canister has reached atmospheric pressure, open the canister valve briefly to release any residual vacuum.
10. Close the canister valve and replace the plug on the canister.
11. Fill out all relevant information on the sample tag for proper recordkeeping. Include all ambient weather conditions in the comments section.
12. Submit the sample to the laboratory for analysis.

In addition to the information on the tag, a chain of custody form is used with complaint monitoring samples. All relevant information must be filled out on the Chain of Custody form.

3.3 Chain-of-Custody

3.3.1 Air Toxics Canister Sample Documentation

An electronic database in the Air Toxics laboratory is utilized as a sample tracking logbook for chain-of-custody. The following information is entered to document tracking of the SUMMA canister transport and subsequent VOC analysis:

1. Initial Laboratory Preparation:

SAMPLE PREPARATION DOCUMENTATION

- Canister Identification, Preparation
- Canister Tracking

2. Field Operations:

SAMPLE PREPARATION DOCUMENTATION

- Canister Identification
- Canister Integrity Verification
- Canister Sampling Data

3. Laboratory Analysis:

SAMPLE ANALYSIS DOCUMENTATION

- Canister Identification
- Canister Integrity
- Login of Sample Information in Database
- Canister Analysis Data
- Data Entry into Database
- Canister Tracking
- Canister Cleaning

3.3.2 Air Toxics Canister Chain-of-Custody Tag

See Attachment #1.

3.4 Analytical Equipment

Various instruments and system setups are utilized depending on the parameters being analyzed. Detailed analytical procedures and components are described in Reference 2, 3, Appendices C, F, and G. Each system is configured to perform analyses based on program requirements. There are two different GC systems for VOC analysis described as follows:

- Analysis of TNMOC is carried out by using a Thermo Trace 1310 GC/FID equipped with a computer with Thermo Chromeleon data acquisition and analysis software. The pressure differential system is used to determine the sample volume. Sample is injected manually. The NMOC analysis is utilized to determine the optimal sample size for subsequent GC/MS analysis.
- The GC/MS system consists of an Agilent 7890 GC with a 5975-C mass selective detector interfaced with an Entech 7200 canister sampler. The GC/MS system uses a DB-1 wide-bore 60m x 0.32mm capillary column to separate the individual compounds. The Entech 7200 system is a 16-position canister sampler interfaced with a GC/MS system for unattended operation. Both systems require programming sequences to operate harmoniously. The Entech 7200 system is designed to pre-concentrate the volatile organic compounds which are present at trace levels in the ambient air samples.

3.5 Calibration Procedures and Frequency

Detailed calibration of the various analytical systems are described in the Air Toxics Section standard operating procedures (see Appendix F) and are briefly described in the following paragraphs.

The Thermo Trace 1310 gas chromatograph used for the determination of total non-methane organic carbon (TNMOC) in all VOC analysis samples is calibrated using an USEPA protocol propane standard containing 0.995 parts per million (ppm) of propane. This corresponds to 2.985 parts per million of carbon (ppmC) because propane has three carbon atoms. This standard is run before the sample is analyzed and the results of a duplicate analysis of the standard must yield a value which is 2.985 ppm +/- 5%. If the calculated value falls out of this range, the instrument is recalibrated using the approved USEPA method.

The Agilent 5975-C GC/MS is used to analyze air samples for TO-15 organic compounds which consist of 62 hazardous air pollutants. The GC/MS system is calibrated using seven levels of a TO-15 NIST traceable standard mixture. A working standard of 5 ppb is prepared from the 1 ppm NIST traceable reference standard. The standard is analyzed on a GC/MS system by varying the trapping volume to establish seven levels of standards. For each compound, three ions are selected based on their abundances. The mass spectrometer software allows one to generate a calibration curve for each target compound. A continuous calibration standard (2.5 ppb) is run with each batch of canister samples to verify the system's calibration. If a majority of the continuous calibration compounds concentrations fall outside the range of 70-130% recovery of the original concentration, the system will be recalibrated again with seven levels of standards and samples will be reanalyzed.

3.6 Data Reduction

The actual sample volume analyzed is determined by a pressure differential system, measured by an absolute pressure gauge:

$$V_s = \Delta P(V_r) / 760$$

Where:

$$\begin{aligned} V_s &= \text{Volume of Sample (ml)} \\ \Delta P &= \text{Pressure Change (mmHg)} \\ V_r &= \text{Manufacturer's Certified Volume of Canister (ml)} \end{aligned}$$

The calculation of the concentration of organic compounds will be performed by the Agilent 5975-C GC/MS. For a fixed sample volume, the concentration is proportional to the area of the quantitating ion counts under the response peak for the compound at the corresponding retention time:

$$\text{Conc. ppbv} = (K) \times \text{area (or counts of the quantitating ion)}$$

Where area is in integrator counts and (K) is an experimentally determined calibration constant (ppbv/count).

The Agilent 5975-C mass selective detector also allows for positive identification of the compound yielding the response peak at a given retention time.

3.7 Data Validation

Sample data may be invalidated for lack of completeness or not meeting criteria for a representative sample. VOC canister sample data validity will be evaluated for the following major monitoring activities:

1. Examples of invalid samples due to lack of completeness:
 - Sampling (elapsed) time differs more than ± 60 minutes from 1440 minutes
 - Broken chain-of-custody (see Section 3.3)
 - Flow instability
2. Examples of invalid samples due to not meeting criteria for a representative sample:
 - Inconsistent sample date
 - Collocated sample volume more than 20% different from reported sample
 - Failure of quality control (QC) checks (see Section 3.8)
 - Canister/sampler not under current certification
 - Failure of QA data validation
 - Flow certification failure
 - Vacuum pressure changed during transport. Pressure difference must be less than 50 mmHg.
 - Unusual events that may affect sample, e.g. vandalism.
 - Failure of precision and accuracy goals

3.8 Quality Control and Quality Assurance

3.8.1 Air Canister Sampling Quality Control/Quality Assurance

General Site Check: This involves sampler and instrument checks at the site. On a monthly basis the site check will be performed by Air Toxics Monitoring Section's personnel.

1. Sampler Assembly Cleanliness Check: This is required every 6 months. The entire sampler assembly will be flushed with hot, hydrocarbon free zero-grade air for two hours at approximately 40-50 cc/min. A certified canister will then be attached and the sampler will be allowed to sample the zero grade air until the canister is pressurized to approximately 10 psig. The canister will then be analyzed by the Air Toxics Section according to the procedure found in Appendix F using a GC/FID system. Cleanliness is defined as <10 ppbC TNMOC.

If a sampler fails the certification then the cleaning process is continued until it passes the certification.

2. **Flow Controller Stability Verification:** This is required every two years. Mass flow controllers for canister systems will be verified for stability every two years by the Quality Assurance Section. Flow rate can't fluctuate more than $\pm 20\%$ in a 24 hour period. An approved NIST traceable bubble meter and stopwatch, or NIST traceable flow meter will be used as the primary standard. For *verification*, two flows are to be taken; one at the beginning of the 24 hour period, and one at the end. The two flows must correlate to the above stated tolerance.
3. **Sample Integrity Logbook Audit:** All canisters must have a final absolute pressure of 15 - 30 psi (22.5 psi is ideal) or the canister sample may be invalid, based upon further investigation by Toxics staff. An elapsed time meter reading of 1440 ± 60 minutes is required or the canister sample is invalid.
4. **Canister Integrity:** Before the sample is taken, the evacuated pressure of the canister will be verified by field personnel to determine canister integrity. After sampling, the sample canister pressure will be verified by laboratory personnel, and it must meet the specifications above to ensure sample integrity.
5. **Elapsed Time Meter Certifications:** These are required every 6 months. Some of these time meters are built-in to the samplers. Depending on the type of Elapsed time meters (ETMs), or other built-in timing device, these will be certified every 6 months by the Quality Assurance Section at ± 1.0 minute tolerance per 24 hour certification test period or these checks can be performed in the field by making sure the date is correct and the time is within ± 5 minutes.
6. **Condensation Control:** This is part of the monthly site check performed by the Ambient Monitoring and Toxics Sections. Water droplets in the manifold will indicate that condensation has occurred. If condensation has occurred, the canister data will be deemed invalid for the appropriate period.
7. **Replacement of or physical trauma to components in any system warrants re-certification.**

3.8.2 Analysis Quality Control/Quality Assurance

Precision: Analysis precision audits will be performed by duplicate independent analysis of a single canister. Ten percent of all samples are projected to undergo duplicate analysis. An Interlab audit will be done once per year by the Toxics Section. Samples will be sent to the USEPA and to the Air Toxics laboratories of other states (Wisconsin and/or other USEPA Region-V states) for replicate analysis. In these cases, calculated concentrations for all components must match within 20% of USEPA results. The Quality Assurance Section will review the results. If any discrepancies in data between the states are found, appropriate corrective action will be coordinated by both sections (Air Toxics and Quality Assurance) to remedy the situation.

Accuracy: Air Toxics personnel will perform analysis accuracy audits by direct analysis of humidified NIST gas standards. Accuracy standards will be analyzed every other analytical run.

Quality Control Standards: Three quality control standards have been provided by the USEPA for the calibration of the VOC analysis equipment. After initial calibration, all systems are checked weekly with at least one of the quality control standards to ensure that the continuing calibration of each instrument meets the USEPA QA/QC guidelines.

Blanks: Blanks are run monthly on all other systems to determine system contamination. In this case, zero is defined as less than 0.2 ppbv per target compound. If it is not “zero”, final data can still be submitted to the AQS database; however, the Air Toxics Section will need to identify the source of contamination.

3.9 Data Precision and Accuracy

Procedures currently used to report precision and accuracy of criteria pollutants are also used to assess precision and accuracy of selected toxic air pollutant species (see Attachments 2 and 3). These procedures conform to 40 CFR Part 58, Appendix A, and “USEPA Quality Assurance Handbook for Air Pollution Measurement Systems Volume 1, Principles” (see Reference 10). Detailed procedures are described in Chapter 13 of the IDEM/OAQ/QA Manual (see Reference 9).

Since no precision and accuracy limits are initially defined, outliers will not be included when audit data is assessed. Testing for outliers will be performed using procedures found in the USEPA Quality Assurance Handbook for Air Pollution Measurement Systems Volume 1, Appendix F. A separate listing of outliers will be maintained and available on request. Outliers will be dealt with according to corrective action procedures (see Section 3.11).

3.9.1 Entire System Precision

The quantitative difference between data duplicate samples will determine the entire system's precision.

3.9.2 Entire System Accuracy

The entire VOC measurement system's accuracy will be determined by the quantitative difference between (1) data obtained by analysis of a canister filled with challenge compounds (NIST standards) drawn through the entire sampling apparatus, and (2) the known values of the NIST gas standards. The quantitative difference between two independent measurements of a single canister sample will determine analysis accuracy. Recoveries of each challenge compound should be 80-120%. Overall system specific recovery (the average of the individual compound recoveries) should be 85-115%. The challenge sample percent recoveries are used to gauge potential additive/subtractive bias characteristics for each specific sampling system.

3.9.3 VOC Analysis Accuracy

The quantitative difference between data obtained using direct analysis of humidified NIST standards and known values of the standards will determine analysis accuracy.

3.9.4 VOC Canister Sampling Precision

Sampling precision will be calculated from the difference in the overall system precision and the analysis precision.

3.9.5 VOC Canister Sampling Accuracy

Sampling accuracy will be calculated from the difference in the overall system accuracy and the analysis accuracy.

3.9.6 Reporting Agency Accuracy and Precision

The precision and accuracy of the reporting agency will be calculated using results from all reporting sites.

3.10 Systems Audits

The State of Indiana Air Toxics Monitoring Program described in this document will be reviewed quarterly by a Total Systems Audit performed by the IDEM/OAQ/QA Section.

Total Systems Audit—performed each quarter;

- Canister/sampler cleanliness records: Make sure the checks are being done every 6 months. The 10ppbC TNMOC limit must be met.
- Canister tag and logbook information check: Make sure 1440 minutes and 15-30 psi for each canister.
- Flow meters, gauges, and ETMs: Make sure each and every one is being checked and certified according to schedule.
- PAMS quality assurance review: NPAP review and Split Sampling outcomes.
- Canister analysis: Interstate Round Robin and NIST accuracy audits.
- Carbonyl Sampling and Analysis: Accurate communication of true flow rate to the contract laboratory and review of USEPA audits performed on the contract laboratory.

Quarterly total system audits will be filed in the Quality Assurance Section. Findings from an audit review will be discussed with the Air Toxics Section on an as needed basis. Results from split sampling, Interstate Round Robin/ NIST accuracy audits and contract laboratory audits will be included in quarterly reports when available.

3.11 Corrective Action

Corrective action may be initiated by field or laboratory personnel with approval from the appropriate lab and field Section Chiefs. Corrective action may also be initiated from precision and accuracy results after review by the Quality Assurance Section Chief.

3.11.1 SUMMA Canisters

Canister Sampling	Limits	Corrective Action
Canister certification	≤ 0.2 ppb of target compounds. Total ≤ 10 ppb	Recertify
Flow controller audit	$\leq \pm 20\%$	Leak check, recalibrate
Vacuum pressure change	$\leq \pm 5\%$ during transport	Replace valve stem
Elapsed time	Outside of 1380 –1500 minute range	Adjust timer/clock
Sampling background	≤ 10 ppbC	Humid zero air system purge

3.11.2 GC/MS Analysis

Criteria	Limits	Corrective Action
QC standards	$\pm 5\%$ from calibration	Recalibrate
Analysis drift	$\pm 10\%$ during analytical run	Recalibrate

4.0 Photochemical Assessment Monitoring Program (Type 2 site)

The PAMS site for the State of Indiana is located in Gary Indiana at the IITRI monitoring site. PAMS monitoring is a mandated program by USEPA as mentioned in the introduction of this chapter. The program requires monitoring of fifty-six organic compounds which are responsible for atmospheric ozone formation also known as ozone pre-cursors compounds. The other species also monitored includes carbonyl compounds, NO_x and NO_y . A Perkin Elmer Ozone Precursor Monitoring System consisting of a Turbomatrix thermal desorption system and a Clarus-500 GC is used for this monitoring which is capable of collecting hourly ambient air samples 24 hours a day throughout the monitoring season. (Note – The Gary IITRI site and the Washington Park site are now operated year-round). The system is programmed for a whole month to collect an hourly sample followed by an automated analysis while the next sample is being collected on an automated thermal desorption (Turbomatrix) unit. The Turbomatrix is designed to pre-concentrate ozone precursor compounds using peltier cooling followed by a desorption of the compounds by heating a cold trap to 325 degrees Celsius in less than 30 seconds to transfer all compounds on to a GC system for the separation. All compounds are separated by dual capillary columns installed inside the GC oven which is temperature programmed for maximum separation. All previous days' data are downloaded via Verizon wireless access card to the Air

Toxic Section's data processing computer first thing in the morning. Data are processed by staff using the "Turbo Chrom" software which came with the PE system. After the data processing, data are imported into LEADS for data validation and AQS file generation. The AQS files are generated for each hour's data files and submitted to the USEPA's main AQS database.

The PAMS monitoring program also requires collection of a 24 hour canister samples every six days throughout the year which is described in the Canister Sampling section of this chapter. For more detail see References 1, 2, 3, 14 and Appendix C.

4.1 Site Selection

Siting must be in accordance with References 6 and 7.

4.2 Sampling Procedures

PAMS canister sampling is conducted using the Air Toxic Monitoring Section's SOP for Meriter MCS-1-R Toxic Sampler (<https://extranet.idem.in.gov/standards/docs/sops/oaq/S-022-OAQ-M-AM-12-T-R1.pdf>)

4.2.1 Remote Sampling

Ozone precursor compounds are monitored remotely using an automated Perkin Elmer Ozone Precursor Monitoring system fitted with an automated thermal desorption (Turbomatrix) device for ambient air sampling. The system is programmed to collect ambient air every hour. After moisture is removed from the air sample by a Nafion dryer, the sample is concentrated in a trap by a peltier electronic cooler. The trap is then ballistically heated from -30 to 325 °C in 10 seconds. The compounds are then purged by helium gas into the Perkin Elmer GC columns.

4.2.2 Canister Sampling

The PAMS monitoring program also requires collection of a twenty-four hour canister samples throughout the year. The canister samples are analyzed using the Ozone Precursor Monitoring System at the Washington Park site. This system is similar to the system located at the Gary IITRI site. Canister samples are analyzed for the same fifty-six ozone precursor compounds as the hourly samples using the same software. In addition to the PAMS analysis these canisters are also analyzed for TO-15 compounds using a GC/MS system for 61 HAP compounds listed in the Title 1 of the 1990 Clean Air Act.

4.3 Chain-of-Custody

4.3.1 Canister Sample Documentation

See Section 3.3.1

4.3.2 Remote Analysis Documentation

No chain-of-custody is necessary since the data is collected remotely via computer.

4.4 Analytical Equipment

The GC's used for speciated PAMS analysis in both the Air Toxics Laboratory and at remote sites are described below.

Remote site monitoring uses a Perkin Elmer Clarus-500 GC/dual FID system. The Perkin Elmer Clarus-500 GC system is equipped with a fused silica $\text{Al}_2\text{O}_3/\text{Na}_2\text{SO}_4$ 50 m x 0.32 mm Plot and a 50 mm x 0.22 mm DB-1 fused silica capillary column.

4.5 Calibration Procedures and Frequency

The Perkin Elmer Autosystem GC system is calibrated for the retention time of each component of interest as well as the response factors used for the quantitation of each compound. This system contains two analytical columns. The calibration of these systems is accomplished using a 56 compound standard made by the Linde Group and provided by the USEPA. The cylinder is certified by the manufacturer. A certificate of analysis is provided by the manufacturer which lists the requested concentration of each compound in the cylinder, the actual concentration of each compound in the cylinder, and the blend tolerance of the cylinder. Two of the compounds present in this standard are propane and benzene. The standard is run five times to determine the average retention time for each compound, as well as the per-carbon response factors of propane and benzene. The per-carbon response of propane is used as the per-carbon response for all compounds which elute from the first analytical column of the instrument (the PLOT column). The per-carbon response for benzene is used as the per-carbon response factor for all compounds which elute on the second analytical column (the BP-1 column).

A continuing calibration check is run every 49 hours on the instrument at the PAMS Type 2 site. The retention times of each component must be within $\pm 2\%$ of the initial average retention time. The response factors for propane and benzene must be within $\pm 20\%$ of the initial average response factors. If either system fails the continuing calibration check, it is recalibrated as described above.

4.6 Data Reduction

The calculation of the concentration of organic compounds will be performed by the Perkin Elmer TotalChrom software. For a fixed sample volume, the concentration is proportional to the area of the quantitating ion counts under the response peak for the compound at the corresponding retention time:

$$\text{Conc. ppbC} = (K) \times \text{area (or counts of the quantitating ion)}$$

Where area is in integrator counts and (K) is an experimentally determined calibration constant (ppbC/count).

4.7 Data Validation

Data validation is done by importing continuous data from the Perkin Elmer AutoGC system into LEADS. The software is designed to flag the data for calibration standard or various null codes to invalidate the data based on system malfunctions. LEADS is also designed to format the data into AQS files for data submittal to USEPA's Air Quality System (AQS) database. Examples of other reasons for invalid data include:

Examples of invalid samples due to lack of completeness:

- 25% of data invalid--on a quarterly, monthly, hourly basis

Examples of invalid samples due to not meeting criteria for a representative sample:

- Response drift > 10% from start to finish of analytical run
- Failure of QC/QA checks
- Failure of QA data validation
- Failure of precision and accuracy goals

4.8 Analysis Quality Control/Quality Assurance

Precision: Analysis precision audits will be performed by duplicate independent analysis of a single canister. Ten percent of all samples are projected to undergo duplicate analysis. An Interlab audit will be done once per year by the Toxics Section. Samples will be sent to the USEPA and to the Air Toxics laboratories of other states (Wisconsin and/or other USEPA Region-V states) for replicate analysis. In these cases, calculated concentrations for all components must match within 20% of USEPA results. The Quality Assurance Section will review the results. If any discrepancies in data between the states are found, appropriate corrective action will be coordinated by both sections to remedy the situation.

Accuracy: Air Toxics personnel will perform analysis accuracy audits by direct analysis of humidified NIST gas standards. Accuracy standards will be analyzed every other analytical run.

Quality Control Standards: Three quality control standards have been provided by the USEPA for the calibration of the VOC analysis equipment. After initial calibration, all systems are checked weekly with at least one of the quality control standards to ensure that the continuing calibration of each instrument meets the USEPA QA/QC guidelines.

Blanks: Blanks are run monthly on all other systems to determine system contamination. In this case, zero is defined as less than 0.2 ppbC per target compound. If it is not "zero", final data can still be submitted to the AQS database; however, the Air Toxics Section will need to identify the source of contamination.

4.9 Data Precision and Accuracy

See Section 3.9

4.10 Systems Audits

The State of Indiana Air Toxic Monitoring Program described in this document will be reviewed quarterly by a Total Systems Audit performed by the IDEM/OAQ/QA Section (see Section 3.10).

In addition to PAMS audits identified in Section 3.10, Quality Assurance staff will randomly select, on a monthly basis, a one hour period of PAMS ozone precursor data for reprocessing. Audit differences of 20 ppbC or more will flag the data for invalidation. If such differences are found, data reprocessing will be required for the previous 12 hours and the following 12 hours. If any 20 ppbC discrepancies are found again, the appropriate hourly data will be invalidated. Reprocessing of 12 more hours prior to and following the previously reprocessed data will be required, and so on, until no more discrepancies are found. Also, if any value higher than 300% of background is detected for a certain hour, that hour will be reprocessed to make sure it is valid.

5.0 Carbonyl Monitoring Program

Carbonyl compound monitoring is conducted using an USEPA method TO-11. Samples are collected on 2, 4 dinitrophenylhydrazine (DNPH) -coated silica gel (Sep-Pak) cartridges followed by an extraction with hexane and subsequent analysis using high pressure liquid chromatography (HPLC) (see References 11 and 12). The carbonyl sampler has the capability for collecting duplicate ambient air samples. Upon completion of sampling, the cartridges are sent to a contract laboratory for analysis. The laboratory performs solvent extractions of the cartridges and analyzes DNPH derivatives of various carbonyls in the extract using HPLC.

5.1 Site Selection

Carbonyl compound monitoring is performed at the PAMS Type 2 site. Site selection must be in accordance with References 6 and 7.

5.2 Sampling Procedures

Ozone interferes with carbonyl sampling, so provisions must be made to remove ozone from the sample path. Either a denuder or cartridge ozone scrubber must be used as part of the sampling apparatus. If ozone scrubber cartridges are used, they need to be replaced every three weeks.

Sampling of carbonyl compounds is carried out by pulling ambient air through cartridges packed with 2, 4-dinitrophenylhydrazine (DNPH) coated silica gel (see References 11 and 12) using an ATEC model 2200 toxic air sampler. The sampler includes the capability for collecting duplicate carbonyl samples. The pre-coated DNPH cartridges are purchased from Waters, Inc.

All exposed cartridges should be refrigerated until time of analysis. Analysis should be performed as soon as possible after receiving the cartridges and no later than 30 days after the sampling date. Performance and logging of calibrations, and the analysis of blanks and spiked control samples will be done by the contract laboratory.

5.3 Chain-of-Custody

The following information is captured for document tracking of the cartridge transport and subsequent analysis:

1. Laboratory:

SAMPLE PREPARATION DOCUMENTATION

- Cartridge Identification, Preparation
- Cartridge Tracking

2. Field:

SAMPLE PREPARATION DOCUMENTATION

- Cartridge Identification
- Cartridge Sampling Data

3. Laboratory:

SAMPLE ANALYSIS DOCUMENTATION

- Cartridge Identification
- Cartridge Analysis Data
- Cartridge Tracking

The paper form for chain-of-custody documentation is shown in Attachment #4.

5.4 Analytical Procedures

Upon completion of sampling, the cartridges are sent to a suitable contract laboratory (Eastern Research Group) for analysis. The laboratory performs solvent extractions of the cartridges and analyzes DNPH derivatives of various carbonyls in the extract using high performance liquid chromatography (HPLC). Cartridges have a refrigerated shelf life of six months; after that, background traces begin to increase. Therefore, any cartridges stored longer than six months will be invalidated.

5.5 Data Validation

1. Examples of invalid samples due to lack of completeness:

- Broken chain-of-custody

- More than 25% of possible data invalid annually, quarterly, monthly, hourly
2. Examples of invalid samples due to not meeting criteria for a representative sample:
- Inconsistent sample date
 - Collocated (where applicable) sample volume more than 20% different from reported sample
 - Unusual events that may affect sample, e.g. vandalism.
 - Failure of QC/QA checks
 - Failure of flow certification
 - Failure of precision and accuracy goals
 - Fails leak check (see Reference 14)

5.6 Analysis Quality Control and Quality Assurance

Quantitative analysis of carbonyl compounds is outsourced to an external contract lab (Wisconsin Occupational Health Laboratory). The contract lab is audited by the USEPA. The Quality Assurance Section will receive the results of the USEPA audits for evaluation and documentation.

5.6.1 Analysis Precision

Analysis precision audits will be performed by duplicate independent analysis of a single cartridge. Ten percent of all samples are to undergo duplicate analysis performed by the contract laboratory.

5.6.2 Analysis Accuracy

Audits of analysis accuracy will be determined by direct analysis of spiked DNPH cartridges by the contract laboratory.

5.7 Sampling Quality Control and Quality Assurance

Flow check audits for carbonyl samplers are performed by Quality Assurance personnel at the end of the PAMS season. The ideal flow rate is 1.2 ± 0.1 l/min. Sampling flow rate will affect the calculated concentration. However, flow rates not within this range are okay, as long as the true flow information is conveyed to the contract lab performing the analysis. If the Quality Assurance flow rate does not match Ambient Section flow rate, troubleshooting must ensue to arrive at a conclusion.

5.8 Corrective Action

Sampling	Limits	Corrective Action
Check Flow	±5% initial reading	Perform leak check. If no leak is found, clean filter/Millipore critical orifice in ultrasonic cleaner. Then perform another leak check.
Perform a final leak check	Leak is detected	Determine location of leak and eliminate the problem.

5.8.1 Carbonyl Sampling Cartridges

Corrective action may be initiated by field or laboratory personnel with approval from the appropriate lab and field Section Chiefs. Corrective action may also be initiated from precision and accuracy results after review by the Quality Assurance Section Chief.

6.0 Lead Analysis Program

Lead monitoring is conducted using an USEPA method EQL-0380-044. Samples are collected on glass fiber filters which have run for 24 hours in a TSP sampler. Information on site selection, sampling procedures, and filter storage can be found in Chapter 7 part 3 of this manual. On October 15, 2008, the USEPA strengthened the national ambient air quality standards (NAAQS) for lead. The current standard is now $0.15\mu\text{g}/\text{m}^3$ for a three month rolling average.

6.1 Analysis Quality Control and Quality Assurance

Filters are analyzed at IDEM utilizing USEPA method EQL-0380-044, or Flameless Atomic Absorption Spectrometry method. Samples are run in duplicate and an average is taken of both readings. When analysis is being performed a 10% standard is run with each set of samples.

6.1.1 Lead Strip Audits

Six lead audit strips are required to be analyzed each quarter. This is comprised of 3 strips at each of two different concentration ranges plus a zero strip to be analyzed with each set of spiked strips. The lower concentration range is 9-30 $\mu\text{g}/\text{strip}$ and the higher concentration is 60-90 $\mu\text{g}/\text{strip}$ of the NAAQS. At this time the strips are prepared by the QA Laboratory at IDEM and sent to several laboratories, however the USEPA is contemplating the possibility of developing the strips for monitoring laboratories dependent upon interest in the program. The six strips are sent out quarterly and 2 strips (one low and one high concentration) are analyzed each month. Results are sent to the QA section and evaluated. If results are greater than $\pm 10\%$ then it is recommended that the system be examined to see if the difference can be reduced. If results are

greater than $\pm 15\%$ then the cause should be determined and should then be reported back to the QA section.

6.1.2 Collocated Monitoring

Collocation of monitors for lead monitoring is required at 1 site for 1-5 samplers, 2 for 6-20, and 3 for more than 20. Collocated samplers run 1 in every 12 days and have a control limit of $\pm 15\%$.

APPENDIX A

Subject: Air Toxics Siting Criteria

General Guidelines:

1. Sampler must be in an area of unobstructed air flow. The distance between an obstruction and the sampler should not be closer than two times the height of the obstruction above the sampler inlet (2X Rule).
2. Location of the site must not be influenced by nearby sources or activities (i.e. exhaust ducts, chimneys, etc.).

The distance from a source, in which emissions are significant (i.e. not representative of the average air quality of the spacial scale to be monitored), is not absolute. The distance depends on chemical stability of the emissions and the detection limit of the monitoring technique. An accepted guideline is as follows:

If the ratio between the estimated source strength (ng/m^3) of the chemical component to be monitored and the actual monitored concentration (ng/m^3) of that chemical component is greater than 10, then that source is having a significant impact on the sample content. The site must be reevaluated.

3. Site must avoid locations where reactive surfaces may cause chemical changes or volatilize and overly represent sample contents (i.e. tar roofs).
4. Site must avoid micro meteorological influences due to nearby hills, bodies of water, valley drainage, airflow patterns, etc.
5. Intake probe must be at representative height (3-15 meters).
6. Probe must extend at least two meters from supporting structures. If located on the side of a building, it must be mounted in the prevailing wind direction. At least a 270° arc around the sampler inlet must be unrestricted and the 270° arc must include the prevailing wind direction for the season of expected highest concentration.

7. Site must be in a high population density area, near sensitive population facilities, or in an area of maximum projected impact.
8. Site must be located on low elevation terrain, where wind flow is not obstructed by prominent buildings and obstructions.
9. Site must be more than 0.5 km from the most dense traffic roads.
10. Site must be downwind from the greatest number of sources or greatest emission density. The highest concentrations will be found downwind from the most stable predominant wind flow direction (0-3 knots).
11. Descriptions and photographs should be prepared and include:
 - Type of ground surface on which the sampler is mounted
 - Direction of and distance from any sources
 - Wind rose showing prevailing wind patterns, and if available, a wind rose for the prominent occurrences of stable atmospheric conditions (light wind of 0-3 knots). These are available from the National Climatic Data Center located in the Federal Building, Ashville, NC 28801.

Specific Spatial Scale Criteria:

- Urban: Impacted by multiple undefined small sources

If the area to be characterized is greater than 5 km², locate the sampler outside and downwind of the source area. If the area is less than 5 km², then locate the sampler within the source area. More than one site is recommended.

- Neighborhood: Impacted by well-defined sources which consist of small areas of industrial or commercial operations, or large integrated plant sites. Locate the sampler in the neighborhood which is downwind from the highest emission density.

APPENDIX B

Procedure excerpt from SOP
S-001-OAQ-M-AT-13-T-R1

Subject: Procedure for Cleaning Canisters

1. Enter the information about the canisters to be cleaned in the canister cleaning logbook.
2. Rotate the cap on the ballast of the precision vacuum pump in the hood and turn on the power switch located at the back of the vacuum pump.
3. Make sure the power to the Variac on the canister cleaning assembly is on in the 120V position and has been set to about 25V. The Variac is connected to the heating tape which will heat the cleaning assembly.
4. Remove the 1/4" plugs from the canisters to be cleaned using a 9/16" open-end wrench.
5. Connect the canisters to the cleaning manifold. Finger-tighten the connecting nut, and then wrench-tighten an additional quarter of a turn. Place the manifold into the oven. Connect the zero air to the manifold and open the valves on the individual canisters. Heat the oven to 90 degrees Celsius.
6. Make sure both valves on the small moisturizer canister are open. This canister contains some HPLC grade water which is used to humidify the zero air used to clean the canisters. Humid zero air is more efficient than dry zero air for canister cleaning.
7. Open the on/off toggle valve on the cleaning assembly by raising it to the "on" position.
8. Open the canister valves by turning them counter-clockwise until slight resistance is felt.
9. Turn the three-way inlet valve slowly so that the arrow points towards the front of the cleaning assembly. The canisters will begin to pressurize with humidified zero air. This will be shown on the absolute pressure gauges. It should only be necessary to open the three-way valve to a 45-degree angle to obtain the optimum rate of canister pressurization for the cleaning.
10. When the absolute pressure gauge reads 30 psi, turn off three-way valve #1 by returning it to its original position (facing absolute pressure gauge). Record the absolute pressure of the system at this point.
11. Wait for one hour and again record the absolute pressure of the system. If the pressure has changed by less than 0.2 psi, the canisters are leak free. If the pressure has changed by more than 0.2 psi, find and repair the leak. Again pressurize the system to 30 psi and repeat the one-hour leak test.
12. Turn the large three-way valve #2 so that the arrow points towards the large copper tubing used for the vacuum transfer line. Turn on the small "rough" (low capacity) pump attached

to the cleaning assembly by turning the power switch on, of the power strip next to the rough pump. Gradually open three-way valve #3 so that the arrow points towards the right-hand absolute pressure gauge. The pressure in the system should begin to drop. When the absolute pressure reaches about 4 psi, the rough pump will become very noisy and will have reached its pumping capacity.

13. At this point, close three-way valve #3 by returning it to its original position (at a 90 degree angle to the vacuum line). Turn three-way valve #2 180 degrees so that the vacuum transfer line from the large precision pump in the hood is now open. Gradually open three-way valve #3 again and the pressure should continue to drop. As the pressure drops, open valve #3 to the fully open position (pointing directly towards the right hand absolute pressure gauge).
14. When the system pressure reaches 0 psi, leave three-way valve #3 open for five minutes to help remove any organics that may be sticking to the walls of the canister.
15. Close three-way valve #3 for the vacuum pump by returning it to its original position (arrow pointing toward the back wall). Turn three-way valve #2 180 degrees so that the vacuum transfer line from the rough pump is again open.
16. Re-pressurize the system to 30 psi as in step #11 and hold the canisters at 40 psi for 3 minutes.
17. Repeat steps 12 through 16 until the canisters have been evacuated a total of twelve times and have then been re-pressurized to 40 psi.
18. Close the valves on all of the canisters. Select one canister and test it for total non-methane organic carbon using the procedure outlined in the following SOP: [Determination of Total Non-Methane Organic Compounds \(TNMOC\) U.S. EPA Method TO-12](https://extranet.idem.in.gov/standards/docs/sops/oaq/S-005-OAQ-M-AT-11-T-R1.pdf)
<https://extranet.idem.in.gov/standards/docs/sops/oaq/S-005-OAQ-M-AT-11-T-R1.pdf>
19. If the average area count is less than 50 (sample contains less than 0.07 ppmC total hydrocarbons), the canister is certified as clean and the relevant data are recorded in the canister cleaning logbook.
20. The canisters are again evacuated to 0 torr and held for five minutes.
21. Close the canister valves and then close the three-way valve to the vacuum pump.
22. Detach the canisters from the cleaning assembly and replace the 1/4" plugs on the canisters. Finger-tighten only.
23. Remove old sample tags from the canisters and replace with new tags found in the drawer labeled "canister label supplies" which is located beneath the cleaning assembly.

24. Place the canisters on the appropriate shelf in the toxics lab.

APPENDIX C

Procedure excerpt from SOP
S-005-OAQ-M-AT-11-T-R1

Subject: Procedure for Total Non-Methane Organic Carbon Determination

The Air Toxics Monitoring Laboratory uses USEPA Method TO-12 for the determination of total non-methane organic carbon (NMOC) in ambient air samples collected by the Indiana Air Toxics Monitoring Network, and in complaint air samples collected throughout the state of Indiana.

These air samples are collected in 6 liter stainless steel canisters which are cleaned, certified, and evacuated prior to use. This cleaning and certification is performed in accordance with our standard operating procedure "Canister Cleaning and Certification"

(<https://extranet.idem.in.gov/standards/docs/sops/oaq/S-001-OAQ-M-AT-08-T-R0.pdf>).

The samples are collected in accordance with either of two standard operating procedures: "Collection of Canister Grab Sample for Toxics Monitoring"

(<https://extranet.idem.in.gov/standards/docs/sops/oaq/S-003-OAQ-M-AT-11-T-R1.pdf>) or

"Toxic Sampler Setup and Pickup Lab Commerce – Meriter MCS-1-R".

(<https://extranet.idem.in.gov/standards/docs/sops/oaq/S-022-OAQ-M-AM-12-T-R1.pdf>)

The analytical method for total non-methane organic carbon determination uses a gas chromatograph with a flame ionization detector to determine the total organic content of an air sample. The gas chromatograph is equipped with 1/16" stainless steel tubing with a 0.007" inner diameter. This tubing is used in the place of a standard GC column because the organic compounds in the sample do not need to be separated. The total organics usually are detected as one peak. Liquid argon is used as a cryogen to trap the organic compounds from a known volume of air sample. At liquid argon temperature, the methane in the sample will not be retained in the trap when the sample is injected onto the column.

The procedure for total non-methane organic carbon determination is as follows:

1. Verify that the sample has been properly collected and the relevant sample data has been recorded in the dedicated laboratory logbook.
2. Verify that the flows on the GC/FID system for NMOC analysis are properly set:
Hydrogen = 30 cc/min, Carrier gas (Helium) = 30 cc/min, Air = 400 to 450 cc/min. These flows are set manually on the GC panel.
3. Verify that the proper programming has been performed on the GC/FID system. The parameters used are as follows:
 - Oven Temp = 150 °C
 - Run Time 0.50 min. Set Baseline

- Report Time 0.50 min. Area Sum on
- Run Time 2.50 min. Set Baseline
- Report Time 2.50 min. Area Sum off
- Run Time 3.50 min. Stop Run
- Detector B on
- Signal B
- Attenuation = 4
- Threshold = 1
- Chart speed = 4 cm/min.
- Annotation on

This programming is performed on the GC Integrator Terminal.

4. Light the FID using the manual igniter switch on the GC/FID system. Verify that the flame is lit using a glass microscope slide. If the flame is lit, moisture will condense on the slide and you will see steam on it.
5. Allow the detector to equilibrate for 10 to 15 minutes before using the system.
6. A 0.995 part per million standard of propane should already be present in a canister in the laboratory. If this standard is not present, obtain a previously cleaned, certified, and evacuated canister and fill it with the 0.995 ppm propane standard located in the cylinder storage area.
7. The concentration of total non-methane organic carbon in the propane standard is calculated in the following manner:

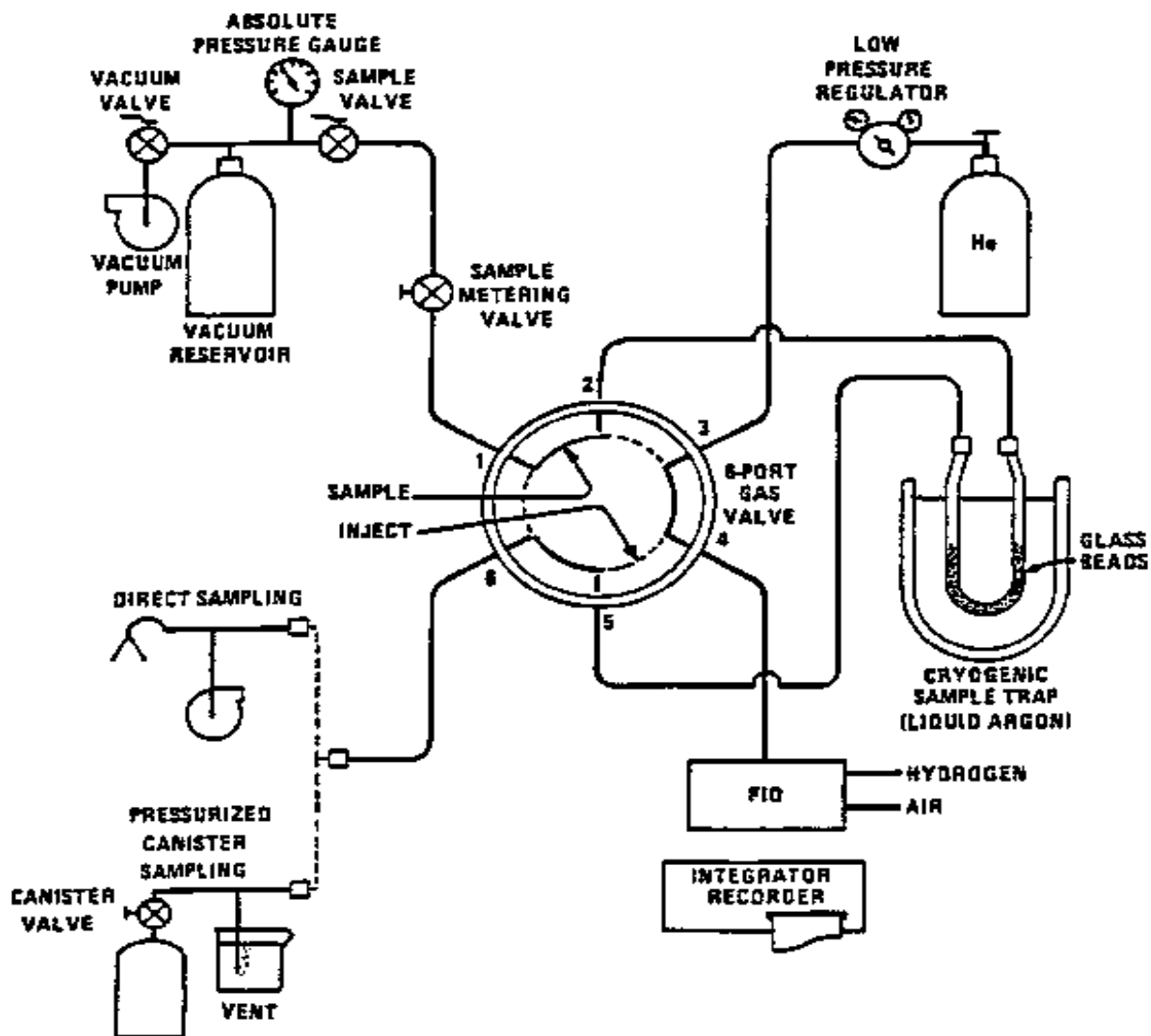
$$0.995 \text{ ppm propane} \times (3 \text{ carbon atoms/propane molecule}) = 2.985 \text{ parts per million of carbon (ppmC)}.$$
8. Initial calibration of the system is performed in the following manner:
 - a. Open the ON/OFF valve on the pressure differential system. Evacuate the small vacuum tank using the floor vacuum pump. It should be possible to evacuate to approximately 50 torr. Turn the ON/OFF valve to the OFF position and turn off the floor vacuum pump.
 - b. Cool the manual trap with liquid argon. It takes 2 to 3 minutes to cool the trap. The Dewar flask maintaining the liquid argon should be supported by means of a wooden block or sturdy box. Use proper safety precautions (safety goggles and insulated protective gloves) when handling liquid argon (safety goggles and insulated protective gloves).

- c. Verify that the switch on the six-port sample injector valve is in the inject position (labeled I).
- d. Hook up the propane standard canister to the sample inlet. Finger-tighten the sample inlet nut and then tighten an additional quarter turn with a 9/16" wrench.
- e. Open the canister valve.
- f. Open the three-way directional valve so that the arrow points directly towards the vacuum tank and the flow goes into the vacuum tank.
- g. Pass standard into the tank until a pressure differential of 10 torr has been seen on the absolute pressure gauge. It should take 30 to 40 seconds for a pressure differential of 10 torr to be achieved. If this time frame is not achieved, it is necessary to adjust the sample inlet flow using the metering valve on the sample inlet. This procedure allows about 25 cc of the standard to flow through the system, but by-pass the trap. In this way, the standard will reach equilibrium in the system before any sample is trapped, thus ensuring consistent results.
- h. Change the switch on the six-port valve to the fill position.
- i. Trap the propane standard until an additional 40 mmHg pressure differential has been achieved. This will trap a volume of approximately 100 cc of standard.
- j. Close the canister valve and the three-way valve (the middle position in which the arrow is at a 90 degree angle with respect to the vacuum bulb is the off position).
- k. Press the Start Run key on the GC Terminal and simultaneously switch the six-port valve to the inject position.
- l. When the first Set BL message appears on the chromatogram at Run Time = 0.50 min., remove the liquid argon from the trap and replace with hot water to desorb the organic compounds from the trap.
- m. Remove the canister from the sample inlet.
- n. Open the three-way valve to the bypass position (pointing directly opposite to the vacuum tank). This will back-flush the trap with 30 cc/min of carrier gas to ensure complete transfer of the standard to the GC. Measure the purge flow at the sample inlet using a flow meter to verify that the flow is 30 cc/min. If necessary, use the metering valve adjacent to the three-way valve to adjust the purge flow.
- o. When the run is complete, the report table will list the area response of the propane standard.

- p. The response factor is calculated by dividing the propane standard concentration of 2.985 ppmC by the area response shown. Response Factor = Conc./Area or 2.985/Area Counts
 - q. Repeat this procedure five times and determine the average response factor
 - r. Enter the value found for average response factor as Calibration -3 on the GC Terminal.
9. Routine daily calibration of the system is performed in the same way as described in (8). However, the average response factor has already been calculated for the system, so it is only necessary to run the propane standard twice. The results for these two runs will be shown in units of parts per million of carbon (ppmC). The average value for the two runs must be 2.985 ppmC \pm 5% for the system to be considered “in calibration”. If the system is not in calibration, step (8) must be repeated.
10. Ambient air samples collected by the Indiana Air Toxics Monitoring Network will have a canister pressure of approximately 1.5 atmospheres (22 psi). These can be analyzed as they are. Complaint samples will have a canister pressure of approximately 1 atmosphere (14 psi). It will be necessary to perform a dilution of these complaint samples using zero air in order to perform the analysis. These samples can be pressurized to 1.5 atmospheres (22 psi) using zero air. The results of subsequent analysis must be multiplied by 1.5 to account for this dilution factor.
11. Sample analysis is performed as follows:
- a. The canister is attached to the system using the 9/16" wrench.
 - b. Water is heated to boiling in a Dewar flask by means of an immersion heater placed on the side of the Dewar.
 - c. The trap is cooled using liquid argon as it was in the calibration procedure.
 - d. With the six-port valve in the inject position, the canister valve is opened, and the three- way valve is opened to the sampling position (arrow pointing directly towards the vacuum tank).
 - e. A pressure differential of 10 torr is allowed to pass into the sample tank in this way so that the sample reaches equilibrium in the system, and then the six-port valve is switched to the fill position.
 - f. A pressure differential of 40 torr (100 cc of air volume) is passed through the trap.
 - g. The three-way valve is closed, and the canister valve is closed.

- h. The Start Run key on the GC terminal is activated, and the six-port valve is simultaneously switched to the inject position.
- i. When the first Set BL appears at 0.50 min. the liquid argon is removed from the trap and replaced with the hot water Dewar. This Dewar is also supported by means of a wooden block or sturdy box.
- j. The canister is detached from the system, and the three-way valve is switched to the bypass position (arrow pointing directly opposite to the vacuum tank) to purge the system.
- k. When the run has stopped, the three-way valve is closed and the hot water Dewar is removed.
- l. The results of the analysis are reported in units of ppmC.
- m. The trap can then be cooled with liquid argon and another sample can be run. Each sample must be run twice, and the reported concentration should vary by less than $\pm 20\%$. If the sample has a fair degree of low boiling point gases, the repeat analysis will usually not be within $\pm 20\%$ of the first one. In this case, the higher (the first) value is accepted. When the analyses are within $\pm 20\%$ of each other, the average of the two is taken. If not, the sample is rerun until more acceptable results have been achieved. It will be necessary to periodically re-evacuate the sample tank to 50 mmHg because the tank will reach the capacity of the absolute pressure gauge on the pressure differential system.

Figure 1
Schematic diagram of analysis system showing two sampling modes



12. The raw data from each sample run is saved in a file folder by sample location and date. The analytical results are recorded on laboratory data sheets and included in the file.
13. The data are then used to either generate reports for complaint samples or input into the AQS database for use by USEPA, State and Local agencies in the case of Air Toxics Monitoring network samples.

APPENDIX D

Procedure excerpt from SOP is S-003-OAQ-M-AT-13-T-R2

Subject: Procedure for Collection of Grab Samples for Air Toxics Analysis

Grab samples of ambient or indoor air are collected in air sampling canisters using a sample probe. The sample probe is made using 1/4" stainless steel tubing which is attached to a flow metering valve and a seven micron particulate filter which is capped with a 1/4" plug. The sample flows through the particle filter and is regulated by the flow metering valve, after which it enters the canister. The canister is cleaned, certified, and evacuated in the laboratory prior to use. The canister valve should be fully closed, and the canister inlet should be capped with a 1/4" plug.

To collect a grab sample, first verify that the canister valve is fully closed. Remove the plug with a 9/16" wrench. Attach the sample probe to the canister inlet. Tighten the 1/4" nut to finger-tight, then use the 9/16" wrench to tighten an additional 1/4 turn. Verify that the flow metering valve on the sample probe is in the off position. Remove the 1/4" plug from the sample probe and open the valve on the canister. At this time, no sample should be entering the canister because the flow metering valve is still closed. If you hear air entering the canister at this time, there is a leak. Close the canister valve and tighten the 1/4" nut at the canister inlet another 1/4 turn. If the system is free of leaks with the canister valve open, open the flow metering valve and set the sample flow so that the sample will be collected in the desired time period. The canister holds 6 liters of air at atmospheric pressure, so a flow of 100 cc/minute would give you a sampling time of 1 hour.

When the canister is close to full, it is necessary to open the flow metering valve to ensure complete sample collection. When the flow meter reads zero with the flow metering valve fully open, close the canister valve. Return the flow metering valve to the fully closed position and replace the plug on the sample probe- finger tight is sufficient for the plug. Remove the sample probe from the canister inlet and briefly open the canister valve to ensure that the canister is full. After closing the canister valve, replace the plug on the canister inlet-- once again, finger tight is sufficient. Record the date, sample time, location, ambient conditions (if sample was taken outside) and other relevant information in ink on the sample card which is attached to the canister. Once this procedure has been completed, the sample can be submitted to the laboratory for analysis.

APPENDIX E

Subject: Procedure for Chain-of-Custody and Sample Logging (Canister System Only)

General Information:

The air samples brought into the laboratory for analysis generally originate from individual complaint. The person bringing in the sample completes a request for analysis form to register the samples for analysis. The custody of the sample is relinquished, the form is signed, and the transfer of the sample chain-of-custody (chain-of-custody form is on the back of the request for analysis form) is acknowledged.

These are usually grab samples and are pressurized to one atmosphere. For analysis, the samples are diluted by pressurizing with zero air to 1.5 times the pressure of the sample when received.

Procedure:

1. Sign the chain-of-custody form. Make and keep a copy of the form.
2. In the sample logbook, assign a sample number and record the source, date of sampling, canister number, and any other pertinent information about the sample.
3. Measure the canister pressure and record in the logbook along with other sample information. If the pressure is at or below 14.3 psi absolute, dilute the sample with zero air to 1.5 times the sample canister pressure. Record the dilution factor (x1.5), final dilution pressure and sample volume.
4. Record the pressures, before and after dilution, on the tag on the sample canister and initial the tag.
5. Repeat procedure 1 through 4 for the next sample.
6. When all samples have been logged in, place the canisters in their proper place.

APPENDIX F

Procedure excerpt from SOP
S-005-OAQ-M-AT-11-T-R1

Subject: Procedure for GC/MS Analysis of Toxic Organic Compounds and Ozone Precursors

I. Introduction:

The GC/MS system is currently used for the analysis of 68 toxic organic compounds found in ambient and indoor air. The monitored compounds are on the USEPA TO-15 monitoring list. The GC/MS system consists of three parts: an Entech 7100A canister autosampler, an Agilent 7890 gas chromatograph (GC) equipped with a 5975-C mass selective detector (MS). These instruments are controlled by a Hewlett Packard Vectra computer which utilizes Hewlett Packard Environmental ChemStation software (version E.02.00.493) as well as Entech Smartlink software (version 1.10). The computer also provides data handling and management for the analytical data generated by these instruments.

The 7100A along with the Smartlink software provides for the sequential analysis of up to 16 canisters plus 3 standards at a time. Due to the unique programmability of this unit, the standard canisters could also be used to provide internal standards, surrogate recovery, or matrix spiking. The Autocan uses an adsorbent trap along with a purge and trap type of moisture control system which allows the removal of water from the sample stream without removing polar organic analytes. This system will allow us to monitor the non-polar toxic organic compounds (USEPA Compendium Method TO-14) as well as polar toxic organic compounds (USEPA Compendium Method TO-15). The sample is transferred from series of 2 traps to a cryofocusing module. After cryofocusing, the sample is directly injected onto the GC column via a heated transfer line.

The GC utilizes a 60 m DB-1 capillary column with a 0.32 mm i.d. The organic analytes are separated on this chromatographic column and transferred to the MS. The MS uses a beam of high-energy electrons to ionize the organic components in the air sample which have been separated on the chromatographic column. The ionized organic molecules are very unstable and rapidly fragment into more stable ions. The MS detects any positively charged ionic fragments of the organic molecules. Each organic compound has a unique fragmentation pattern which can be identified with a very high probability. This unique aspect of mass selective detection allows for positive identification of the organic compound by retention time and by fragmentation pattern; whereas, most chromatographic detectors only identify compounds by retention time. GC/MS data is often referred to being three-dimensional because the GC/MS provides retention time, mass spectra, and quantitation data. The mass spectra of each compound in each air sample is compared to the known spectra of organic compounds in the database, and a probability of the best match is generated.

The system is calibrated using a 68 compound TO-15 standard which is obtained through Air Liquide or Linde. Other compounds may be added to our monitoring list as calibration materials become available. The standards are run on the GC/MS at three different concentration levels to generate calibration curves for each component.

II. Operating Conditions:

The GC/MS system is more difficult to operate than conventional GC/detector systems due to the difference in operating environments between the GC and MS. The gas chromatograph ideally operates at ambient temperature and pressure with a column flow of 2 to 5 cc/min. The MS operates ideally under high-vacuum conditions with an optimal flow input of zero. To compensate for the differences in operating conditions, the GC/MS interface is used. The GC column is inserted into the interface and the connection is sealed using a 0.5 mm i.d. Vespel ferrule and a brass interface nut. The connection of the Entech 7100A heated transfer line to the GC column at one end, and the connection of the GC column to the GC/MS interface at the other end are the most common sources for leaks in the GC/MS system. They must be carefully checked to ensure there is no air leaking into the system. Any air leaking into the system will interfere with the quality of the chromatographic analysis and will cause oxidative contamination of the mass spectrometer ion source, thus causing further degradation of chromatographic quality. If chromatographic quality degrades significantly, the ion source must be carefully cleaned according to the procedures outlined by the manufacturer.

GC column flow is set in the GCMS method file to 1.5cc/min. The proper GC column dimensions must be identified in the software in order for the flow calculations to work correctly. This flow is an acceptable compromise for the GC that ideally operates from 2-5 cc/min and the MS which ideally operates with a flow of zero.

III. Tuning the Mass Spectrometer:

Once the GC/MS system has been shown to be free of leaks, and all of the flows have been set to the appropriate values, the mass spectrometer must be tuned. The mass spectrometer is tuned using the compound perfluorotributylamine (PFTBA). This compound contains no hydrogen atoms, and therefore has no mass defect (hydrogen causes a mass defect because it has an atomic weight of 1.008 amu instead of 1.000). This compound has a characteristic fragmentation pattern with a base peak of 69 amu and significant peaks at 131 amu, 219 amu, and 502 amu. There are other peaks at 264 amu and 404 amu which are occasionally used for special tuning applications. The standard autotune and maximum sensitivity autotune routines use the 69, 219, and 502 mass peaks to tune the instrument. Tuning the mass spectrometer accomplishes the following tasks:

- It sets the voltages of the various lenses in the ion source and the quadrupole mass filter so that only the desired ions reach the electron multiplier and are detected.
- Tuning sets the voltage of the electron multiplier so that the ions detected give an appropriate level of signal.
- Tuning adjusts the mass axis so that detected fragments will be assigned the proper mass.

These adjustments made during the tuning process ensure that data obtained on the GC/MS will have the optimum sensitivity, the proper resolution, and the correct abundance for quantitation.

A standard spectra autotune is performed every time the instrument undergoes any significant maintenance. This tune generates a report which is saved as a .pdf file. Prior to any sample analysis, a tune evaluation is performed. The tune evaluation is an automated procedure which verifies that the current tune file. The results of this tune are used to gauge the general performance of the mass spectrometer. The presence of large mass peaks at 18 amu (water) or 28 and 32 amu (air) indicate a leak in the GC/MS system. The leak must be found and eliminated. For further discussion of detecting and eliminating leaks in the GC/MS system, refer to the section of this document entitled "GC/MS Maintenance".

Target Tune is used to generate the parameters for the BFB Tune Criteria. The targets used are as follows: Peak Width = 0.50, 131 = 45% of 69, 219 = 45% of 69, and 502 = 1.2% of 69. The results of the current Autotune are loaded as the starting point for the Target Tune, and Target Tune is run. The Tune Targets are stored in a file named BFB.TGT and the Target Tune results are stored in the file BFB.U. The Target Tune program takes the parameters from the Maximum Sensitivity Autotune and continuously adjusts the ramps of all lens parameters until the desired targets are met. The results of the Target Tune are also in the MS Tune Logbook.

The reason for all of this elaborate tuning is so that 4-bromofluorobenzene can be introduced into the system as a tune check for volatile organic compounds and will meet the criteria given by the USEPA for ion abundances. The 4-Bromofluorobenzene is present in our GCMS internal standard cylinder along with 3 other compounds used as internal standards for our calibration methods. The stock (cylinder) standard contains these four compounds at a concentration of 1ppm. The Entech 4600A dynamic dilution system is used to prepare a working standard of the internal standard mixture at a concentration of 10 ppb. This standard is then used to assess the quality of the BFB Tune of the GC/MS system. 125 mL (which contains approximately 50ng of BFB tuning compound) of the internal standard mixture is trapped on the Entech 7100A and injected onto the GCMS system and run using the current data acquisition method.

After the data acquisition is complete, it is necessary to evaluate the mass spectrum of the apex of the peak corresponding to BFB for compliance with the USEPA environmental tuning requirements. If the tune evaluation fails, it is necessary to manually analyze the data to ensure compliance with USEPA requirements for BFB tuning. From the Environmental Top screen, click on View, and Click on Data Analysis. From the data analysis menu, choose File, Load Data File, and choose the name of the file which contains the BFB data for the run just completed. This should bring up a Total Ion Chromatogram of the run. Go to the Tuner menu and select Auto-Find BFB to Screen. The Auto-Find BFB function will automatically locate the BFB peak, average the 3 spectra nearest the apex of the peak (the apex scan, one scan prior to the apex, and one scan after the apex), and will also automatically subtract a background spectrum from the baseline of the chromatogram. A report is automatically generated on the screen, which will show the USEPA requirements for passing a BFB tune and will evaluate your spectrum compared to these requirements. If everything has been done correctly, the standard should pass all of the requirements. If the spectrum fails, it is acceptable to use the single scan at the apex of the BFB peak and evaluate it manually.

When a scan has been located which passes the BFB tune requirements, go to the Tuner Menu and select either “Auto-Find BFB to Printer” (if the Autofind procedure was successful) or “Evaluate BFB to Printer” (if a single scan at the apex of the peak was used). Once the BFB standard has passed the tune check requirements, the system can be calibrated. If the standard will not pass the USEPA requirements, it is necessary to go back and redo the Target Tune procedure. If target tuning of the MS is not sufficient to allow the system to pass the BFB tune requirements, it is necessary to manually tune the instrument to ensure that BFB tuning requirements are met. Manually tuning the instrument is a very complex procedure which should be performed by an experienced MS user. This process will provide the instrument with maximum sensitivity for passing the BFB tune check. If the instrument still does not pass the BFB tune check, it is possible that the Ion Source requires cleaning or the PFTBA vial may need to be refilled. Consult the GC/MS Hardware manual for instructions, or consult Hewlett Packard customer support to set up a service call for the instrument if source cleaning and refilling the PFTBA vial do not solve the problem. Instructions for source cleaning, refilling PFTBA, and other routine maintenance can also be found in the GC/MS SOP.

When BFB tune requirements have been passed, it is then necessary to calibrate the instrument.

IV. Data Acquisition I: Method Generation for GC/MS Calibration and Sample Analysis

In order to acquire GC/MS data, it is necessary to build methods which set the GC and MS parameters and data handling requirements so that relevant, reliable data is collected and stored on the Chemstation. Building a data acquisition method allows the user to specify the mode of acquisition (SCAN or SIM), the Tune file used to set MS tuning parameters, MS acquisition parameters (scan range, sampling rate, and threshold), GC acquisition parameters, and injection parameters.

When a method is created, it is stored on the Chemstation hard drive in the directory C:\HPCHEM\1\METHODS with an .m extension on the filename. The user may create any number of methods for differing data acquisition needs. The data files created by running a method (performing an analysis) are stored in C:\HPCHEM\1\DATA with a .d extension on the filename. Methods also entail the data analysis portion of the analytical run, but for practical purposes, data acquisition and data analysis will be treated as two different sections. For a full discussion of all aspects of data acquisition method development, refer to the course manual H4050A Environmental GC/MS-DOS Operation, Volume 1, Section 4 from Hewlett Packard.

The method files for the GC/MS and the Entech 7100A have already been created and stored on the hard drive of the computer; however, it is necessary to know how to regenerate these methods in case of a catastrophic system failure. The first step in creating the method is to start by loading the default method file C:\HPCHEM\1\DATA\DEFAULT.M into memory. This is accomplished from the GC/MS instrument control screen by clicking Method → Load, and selecting DEFAULT.M from the appropriate directory.

The method is edited in a series of panels which are filled out by the user. To begin the editing process, click on Method and select Edit Entire Method. Select all three method sections to edit (Method Information, Data Acquisition, and Data Analysis). This method file can now be used to acquire the data needed for instrument calibration.

It is now necessary to sequence the GC/MS and the AutoCan to perform the initial calibration of the instrument. An initial calibration of the instrument is necessary whenever any tuning parameters on the instrument are changed in order to pass the BFB tune check, or whenever the instrument is otherwise out of calibration.

Because it is easier to acquire the data for the calibration of the GC/MS sequentially using the Entech 7100A, it is now necessary to use the procedure for sequential data acquisition using the 7100A and GC/MS.

V. Data Acquisition II: Sequential Data Acquisition for Calibration and Sample Analysis

The Entech 7100A Canister Autosampler allows for the sequential analysis of up to 16 canister air samples along with up to three standards. The following procedure will outline the necessary steps for performing sequential GC/MS analysis using the 7100A.

1. Perform a Tune Verification of the mass spectrometer. Observe the printout of the tune report. If there are peaks above 5% of the 69 amu peak for mass 18 (water), or above 10% of the 69 amu peak for masses 28 or 32 (air), a leak in the GC/MS is indicated and must be fixed. If the EM Voltage exceeds 2499 mV, the source may need cleaning, or the PFTBA valve may need to be refilled. Consult the GC/MS SOP as needed.
2. Load standard and sample canisters onto the 7100A.
3. Keep all canister valves closed initially.
4. Select set-up, leak check from the Smartlink menu.
5. Select system plus all used canister positions for the leak check; Press the "Go" button to begin.
6. Review the QA/QC report from the leak check and tighten any loose fittings.
7. Perform leak check again if necessary.
8. Print the leak check report to the CutePDF writer. Save the .pdf file with a unique filename containing the date on which the test was performed.
9. Write a sequence using the Smartlink software to run the standards and samples on the rack.

10. Select File → Save and give the sequence an appropriate name containing the date on which the sequence is being run.
11. Save a .pdf copy of the sequence by printing the sequence to the CutePDF writer. See untitled attachment 2 for an example.

If the sequence is for an initial calibration of the GC/MS, BFB and nine levels of the appropriate standard (10 cc, 25 cc, 50cc, 100cc, 200cc, 250cc 300cc, 500cc, and 1000 cc) should be sequentially sampled using the autocal. If desired, a canister containing humidified zero air can be attached to the 7100A at port 16, and this canister can be sampled and analyzed after each calibration run in order to verify that the Autocal and GC/MS are not experiencing any sample carry-over from one run to the next. If sample carry-over is observed, consult an Entech service engineer for help trouble-shooting the autosampler.

The GC/MS must also be sequenced in order to properly acquire the sample data. Select Start → Programs → GC/MS Instrument #1 to start the GC/MS. The previously loaded method will automatically load. Use the Windows Taskbar to access the MS Top menu screen. Select Sequence → Edit Sample Log Table to create the GC/MS sequence.

Once the sequences have been written and sent, it is necessary to click the Go button on the 7100A software screen in order to start the runs. It is also necessary to run the GCMS sequence which has been created. The 7100A sequence and the GCMS sequence can be started simultaneously. Once the GC/MS and 7100A have started, the sequence will continue until complete. The GC/MS will automatically load the DEFAULT.M method following all sequenced analytical runs. The oven temperature in the default method is set to 70 °C, so no liquid nitrogen will be used once all runs have completed.

VI. Data Analysis I: Initial Instrument Calibration

After the sequence of calibration runs have been run, the Chemstation will have data files for each run which have been quantitated using default parameters. It is necessary at this point to identify all target peaks in the calibration chromatograms, and provide quantitation information in the method to generate 3-point calibration curves for the method. From the instrument control or MS Top menus, click on view and select Data Analysis. Use the following procedure to perform the initial calibration of the GC/MS method:

1. Click on File.
2. Click on Load Data File.
3. Select the data file for the mid-level calibration run (250 cc trapped).
4. If the method file shown in the Window title-bar is not the most recent TO-15 calibration method, click on File, select Load Method, and select the most recent calibration method as the method file.

5. Go to the InitCal menu and choose SetUp Quantitation. A panel for entering quantitation database globals will be displayed. Enter TO-15 calibration as the Calibration Title. Leave the default multiplier at 1.000 and set the default concentration amount to 5.000. In the area labeled Locating Peaks, set both the reference and non-reference windows to 1.000 minutes and set the correlation window to 0.05 minutes. Make sure the Use RTEINT Checkbox is checked. In the area labeled New Compound Info, choose RTEINT.P as the integration parameter file, set the default to ± 0.500 min around exp RT, choose Average of Response Factors for the curve fit, select Area as the parameter to measure, enter PPBC as the units of concentration, and leave the ISTD concentration set to 0.000 since this method does not make use of an internal standard. When these entries have been completed, click OK.
6. Next, the Edit Compounds panel will be displayed. Highlight the [END OF COMPOUND LIST] and click Insert Above. The Total Ion Chromatogram (TIC) of your data file will again be displayed.
7. Enlarge the first few minutes of the TIC by positioning the cursor at the lower left baseline of the chromatogram. Press and hold the left mouse button and drag the cursor over the region of the TIC you wish to "zoom in" on. When the mouse is dragged, the outline of a box should appear on the TIC. When the desired region all falls within the box, release the mouse button. The selected region will be enlarged to fill the chromatogram window. This procedure makes it easier to select the apex of the peaks of interest for the calibration.
8. Select the first peak of the chromatogram by positioning the cursor at the apex of the peak and double-clicking the right mouse button. This will cause the mass spectrum of the apex of the peak to be displayed below the expanded TIC, and a panel labeled Quant Setup will appear to the right of the mass spectrum.
9. Select the Lib option from the top menu bar and choose Select Library.
10. Enter a ? (question mark) when the library name is requested. This will display a list of available libraries.
11. Select the NIST compound library from the list. It will now be possible to identify the mass spectra from the TIC by library searching.
12. Position the cursor anywhere within the mass spectrum window and double-click the right mouse button. A list of the library search results will be displayed. The first search result is generally the correct choice for compound identification. A list of the compounds present in this standard has been provided by Scott Specialty Gases, and Tekmar has provided a GC/MS chromatogram of this standard to aid us in our calibration. Consult the compound list to verify that the first peak is a compound of interest in the standard. The first target compound on the chromatogram should be Freon-12. If the current peak is not identified as a compound of interest, proceed to the next peak on the TIC.

13. When a compound of interest has been located, enter the name of the compound in the Quant Setup window.
14. Select the target ion used for quantitation by positioning the cursor on the ion you wish to use as the target ion (the cursor will appear as a target site) and simultaneously click the left and right mouse buttons. NOTE: the most abundant ion should generally be selected as the target ion for the most repeatable quantitation results.
15. Next choose at least one qualifier ion (up to three may be chosen). The qualifier ions chosen should include the molecular ion and any ions which are characteristic of the molecule. For example, for benzene, the target ion chosen would be 78 amu, and the qualifiers would be 77 and 50. Once all of the data is entered in the Quant Setup panel, click on Save.
16. Go to the next peak on the TIC and repeat this process. When necessary, zoom out on the TIC by double-clicking the left mouse button anywhere on the TIC and zoom in on the next region of interest. Repeat the above steps until all compounds have been entered into the calibration database. Refer to the flow chart copied from the Hewlett Packard 4050A course manual.
17. After the data for the last compound has been saved, click Exit to return to the main menu.

(Note: Steps 5-17 only need to be performed if the instrument has never been calibrated before. If there is an existing previous calibration, steps 5-17 are unnecessary.)

18. From the InitCal menu, choose Update Levels. This will display the Update Calibration Panel. Select Add New Level using Calib Level ID 5 (5 ppb/compound). Select 5 for the Cmpd Conc, and leave the ISTD Conc. at 0. Click on Do Update. At this time, the message "This file has not been quantitated... quantitate now?" may appear. If so, select Yes. The data file will be quantitated, and the quantitation data will be added to the quantitation database.
19. After the first quantitation level is added, it is necessary to edit the compounds and change their amounts. Use the certificate of analysis (COA) provided by the standard cylinder vendor to enter the exact amounts.
20. Now go to InitCal and select Global Update. Select Set Subtraction Method and choose Extended Area Quant. Also from the Global Update menu, set the identification method to Best RT Match. Then from the Global Update menu, choose Set Other (via command) and enter the command Unc Tp=0 to change the % uncertainty for the qualifier ion relative responses to 20% absolute (as specified by the USEPA). This step is only necessary the first time the instrument is calibrated. If an existing calibration method is being updated, this step is not necessary.
21. The USEPA specifies a minimum of five points used in the calibration curve for this method. We use a total of 9 calibration levels to verify the linear calibration range of the

instrument from 0.10 ppb up to 10.0 ppb, so the other seven levels of calibration standard are added to the calibration table. It is much easier to add these levels to the calibration table however, because all of the retention time and target/qualifier ion data has been previously entered. All that is needed is to load the data file and select InitCal, Update Levels. Choose Add New Level using the appropriate Calib Level ID for each level of standard which has been run. Click on Do Update. Once again the message "file has not yet been quantitated... quantitate now?" may appear. Select yes. Then edit the compounds to reflect the exact amounts calculated from the COA provided by the standard cylinder vendor.

22. Once all nine levels have been added to the database, load the 250 cc data file again. Go to InitCal, Update Levels and again select Add New Level. Name this level CC. It will be used as the continuing calibration level to check that the calibration table is remaining valid over time. Once again, edit the compounds using the COA provided by the vendor.

Now the GC/MS system is calibrated for this method. Check that the calibration curves for each compound are roughly linear by going to the Edit Compounds menu and double-clicking the left mouse button on the first compound. Go to page two of the calibration information and view the plot. The calibration curve will be displayed. The curve should be within 15% of linear. Choose Next Compound and check the next curve. Repeat until all curves have been checked. If any calibration curve exceeds 15% from linear using the Average of Response Factors, it is acceptable to change the curve fit to Linear Regression forced through Origin. If this curve fit is used, the correlation coefficient should be >0.984 . If a good linear curve fit cannot be achieved using either method, it is acceptable to use a quadratic curve fit, but the correlation coefficient for a quadratic fit should be at least 0.99. Data for any compounds which use quadratic curve fits should be carefully examined to verify consistency with previous data. If none of the linear or quadratic curve fits yield acceptable results, the calibration is not valid for any compounds failing to yield acceptable calibration curves. This indicates a problem with the system which should be investigated and resolved before the instrument is used to run samples. Following resolution of the problem, the system may need to be re-tuned, and will need to be recalibrated. Make sure to SAVE the method before exiting the data analysis software. HP's software has the annoying habit of saying "Be sure changes are saved... Exit Now? Yes/No". If you choose yes to this option, your changes to the method are NOT SAVED!!!!

VII. Data Analysis II: Sample Data Analysis and Report Generation

Sample analysis on the GC/MS system is remarkably easy once the methods have been created and calibrated. Determine the total NMOC concentration of the sample using the GC\FID NMOC system. If the total organic content of the sample is less than 2 ppmC (parts per million of Carbon) as determined on the GC\FID NMOC system, 500 ml of the sample is trapped for the analysis on the GC/MS system. If the sample contains more than 2 ppmC total organic compounds, the sample is either diluted with hydrocarbon-free air to achieve desired concentration or less sample (250 ml, 100 ml, or even 50 ml) is trapped to avoid overloading the mass spectrometer and possibly contaminating the ion source. In the case of the Gary IITRI canisters, the sample is also analyzed for speciated organic compounds on the Perkin Elmer Ozone Precursor system located at Washington Park.

Sample data is acquired using the steps in Section V of this document. If these steps are followed correctly, result files for BFB, at least one level of standard, and all sample data files should be generated. BFB should be run at least once every time a sequence is run in order to ensure that the instrument is still meeting USEPA tune requirements. A mid-range standard should also be run with each sequence to verify that the instrument is still in calibration. The data file for the calibration standard should be compared to the continuing calibration level in order to verify the calibration of the instrument.

The data files generated for each sample are acquired sequentially using the Teklink sequence to control the Tekmar Autocan unit and the GC/MS sample log table to control data acquisition on the GC/MS. The data files can be quantitated automatically as part of the GC/MS method; however, it is necessary to review the quantitation of each chromatogram to verify correct peak identification and integration. In order to prevent the print-out of GC/MS summary reports for data files which have not been verified and validated, do not select any destination for the report when creating the method (leave the check-boxes for screen and printer blank when specifying the destination for the summary report). This will cause a QUANT.RES file to be generated for each sample chromatogram without printing the quantitation report.

Select QEdit Quant Results from the Chemstation data analysis menu. A list of the calibrated compounds for the selected method will appear at the top left of the screen, and the remainder of the screen will display windows showing the first target compound found for the selected data file, as well as the integration and quantitation information for the given peak.

To reintegrate a peak, which has been integrated incorrectly due to noise or other interference, move the mouse pointer to the lower left baseline point of the peak. Click the right mouse button and drag the pointer to the desired right baseline point for the peak, and release the mouse button. This procedure will cause the peak to be reintegrated, and the new peak area will be displayed in the lower right window on the screen which shows the area and qualifier ion relative responses. When a report is generated, the quality match for this peak will be displayed with an "m", indicating that the peak was manually integrated.

To re-identify a target compound which has been erroneously associated with a nearby peak, move the mouse pointer to the apex of the peak which is suspected to be the target compound. Double-click using the right mouse button on the peak apex; this will cause the mass spectrum of the compound corresponding to this peak to appear in the lower window. To perform a library search for the identification of the compound in question, move the mouse pointer anywhere inside of the mass spectrum window and double-click the right mouse button. A series of possible identifications for the peak will be displayed near the bottom of the screen, with the compound having the probability of best match displayed first. If this peak matches the suspected target compound, use the above-mentioned manual integration procedure to identify and integrate the peak.

When the first peak has been verified as being identified and integrated properly, repeat the verification of peak identities and proper peak integrations for all of the target compounds.

When the integration and quantitation of the chromatogram have been completed, click on file, and select Exit and Save Changes. Doing this will save any new information in the QUANT.RES file for the given sample and will exit the Q-edit function.

To generate a summary report of the data analysis for a given sample, click on Quant and select Generate Report. DO NOT select Calculate and Generate Report. If Calculate and Generate Report is selected, any manual identification and integration which was performed using the Qedit procedure will be eliminated. The generated report will contain the data file name, the date, any additional information which was specified in the sample log table, and a tabulation of identified target compounds, the quantitation of each compound, and a percent match with the compound library. This data can then be entered into the appropriate database.

VIII. Data Validation and Quality Control

All GC/MS data must be validated as shown in the previous section in order to be deemed acceptable data. The following data validation and QA/QC steps must be performed in order to ensure the quality of the data generated by the instrument:

1. Perform a Tune Verification before each sequence and save the tune results. The results should be examined for the presence of air and water in the system (indicating a leak), and for the EM Voltage needed to tune the instrument (increasing EM Voltage indicates either a dirty ion source or the need to replace the electron multiplier).
2. Save the BFB Tune Check results. The instrument must pass the BFB tune check before each sequence. Failure of the BFB test indicates the need to re-tune the instrument or possibly the need for instrument maintenance. If the instrument is re-tuned, it must also be recalibrated.
3. Save the results of initial and continuing calibration files. The continuing calibration check should be within $\pm 30\%$ for each compound (a few compounds with small peak areas may exceed this limit, vinyl chloride being a good example). If the continuing calibration check fails, the initial calibration must be performed again.
4. Document any instrument maintenance performed by Air Toxic staff or by an Agilent service engineer in the instrument log book. Also document any maintenance performed on the Entech 7100A. Perform routine maintenance annually as specified in the GC/MS preventive maintenance schedule.
5. Document any invalid sample results and note the reason for invalidation of results in the appropriate database.

IX. Conclusion

The GC/MS with the Tekmar Autocan canister autosampler is an extremely complex system used for the analysis of ambient and complaint air monitoring samples. This SOP is an attempt to

summarize the techniques of air sample analysis using this instrumentation. Thorough training in these techniques as well as the maintenance and care of this instrumentation is necessary to ensure the quality of analytical results. This procedure is not intended to be exhaustive, but should provide a general step-by-step procedure for obtaining quality data.

APPENDIX G

Subject: Select Air Toxics Procedures and Guidelines

Procedure excerpt from future SOP

A. Procedure for Restarting an Autosystem GC Sequence after Failure

If the sequence on the Perkin Elmer Autosystem GC Ozone Precursor Monitoring System has been interrupted, it will be necessary to re-start the sequence at the proper sample number as soon as possible after the interruption has been detected. To re-start the sequence, the following procedure is used:

1. The sampling must resume on the next possible hour. Check the current time and convert the time of the next hour into military time. Note that all sampling is conducted on local standard time, and that the computers at each site should be set to local standard time throughout the year.
2. Consult the calendar and add the military time you have just determined to the number shown below the appropriate date to determine the row number at which the sequence should be started.
3. If the Totalchrom Navigator is not open or if the computer is not functioning properly, reset the computer. The Turbochrome Navigator will start automatically after the computer boots.
4. Click on Analysis Setup from the Navigator. Under Setup Type, choose Sequence.
5. Under Sequence, use the following pattern for the current month.

October = "C:\TC4\Gary IITRI\Sequences\October.seq"

November = "C:\TC4\Gary IITRI\Sequences\November.seq"

or

October = "C:\TC4\Washington Park\Sequences\October.seq"

November = "C:\TC4\Washington Park\Sequences\November.seq"

6. For the starting row, enter the starting row which you have previously calculated (e.g. 2:00 pm. on June 9th = $14 + 193 = 207$).
7. For the ending row, enter 720 for a 30 day month or 744 for a 31 day month.
8. Under Interface Data Buffering, select Multiple Runs.
9. Make sure the Check box for Suppress Reports and Plots has an X in it (if not, click on it with the mouse).

10. Click on OK. This will load the sequence.
11. Make sure that the Turbomatrix is in Standby Mode and the GC is ready.
12. At 2 minutes prior to the start of the hour, press Start on the Turbomatrix (this starts the sequence).
13. Make sure that the ATD-400 loads the tube and proceeds to the Leak Check. The leak check and tube purge take 2-3 minutes, so if the sequence was started 2 minutes prior to the top of the hour, sampling should commence at the top of the hour.

B. Remote Access of PAMS Computer

The field computer receiving data from the Perkin Elmer system at the remote site is known as HOST. The computer at the Indianapolis laboratory is known as REMOTE. Remote access to the HOST computer is achieved using the remote desktop feature in Windows XP. Control of the HOST computer may be necessary to modify a method or modify a sequence or simply to delete temporary files.

C. Instructions for Manual File Transfer from the remote PAMS Site (Host Computer) to the IDEM Laboratory (Remote Computer).

The raw data files from the site will be transferred automatically to the directory D:\ARCHIVE on the data storage drive on the IDEM lab computer (the one you are working on). For 24 hours of data files, it takes about 15 minutes to complete the transfer. There are two files per hour, so a total of 48 files should transfer. This script will also automatically erase all data files in the download directory of the host computer after they have been transferred and will delete any .tmp files in the TEMP directory of the host computer.

If all files have transferred successfully, this procedure is complete. If there was a problem with the data transfer, it will be necessary to retrieve the data from the data drive at the site. There are several ways of doing this. The easiest way is to take control of the host computer at the site using the procedure for accessing the field computer. Use the file manager to copy the appropriate files from the data drive of the host computer back to the C:\DOWNLOAD directory. Terminate the session and then repeat this procedure.

Note: The scheduler is set to perform the file transfer and deletion automatically at 12:15 a.m. every day. It is necessary to verify the file transfer every morning. If any errors in transfer have occurred, it will be necessary to connect to the host computer and transfer any missing files as described above.

D. Blanks and fifty-six Component Calibration Checks at the PAMS Type 2 Site

In order to meet the system check requirements for PAMS Type 2 Site Ozone Precursor Monitoring, we have chosen to run a full 56 compound calibration standard Every 49 hours automatically as part of the monthly sequence. On the first day of the month, the calibration standard is run at sampling hour 0 (zero), on the third day of the month the calibration standard is run at hour 1, etc.

E. Validating VOC Data from the Perkin Elmer Autosystem GC System

1. To verify the retention times for a GC system it is important for the system to be operated for a period of 2 to 5 days to allow equilibrium and retention times stabilization.
2. It is very important that standards be prepared in humidified air, at a relative humidity similar to the samples being analyzed.
3. Peak identification by retention time is adequate for the PAMS network requirements.
4. Periodic confirmation of peak identification and quantification using more definitive techniques such as GC/MS is encouraged.
5. To account for any retention time variations, relative retention time (RRT) can be used to aid in assigning peak identifications.
6. The use of reference peaks in several retention time windows is recommended to compensate for retention time shifting that is not linear. Suggested reference peaks include toluene, benzene, and butane.
7. Blank samples that contain humidified zero air should be analyzed to establish the GC system background readings and determine level of contamination or artifacts. Blank or zero air samples should not contain the target VOC's at a concentration greater than the detection limits.

There is a requirement for Zero or Blank runs. A series of blanks including a GC oven blank, a trap blank, a system blank, and a humidified zero air blank are run twice per year (usually in April and October). This series of 4 blanks is described in the current PAMS SOP. Additional humidified zero air blanks may be run at any time throughout the year if contamination of the system is suspected for any reason.

F. Detection Limits

The detection limit is defined in the CFR as the minimum concentration of a substance that can be measured or reported with 99% confidence that the analyte concentration is greater than the zero air concentration as determined from analysis of a sample in a given matrix containing the analyte.

All results, even concentrations below the estimated detection limit, should be reported. Valuable information is recorded when a result is reported even if the data is somewhat imprecise. All concentrations must be reported in ppbC.

G. Chromatography Result Report File Review

All chromatograms generated by the system should go through a cursory review by the station operator to determine if the quality of the chromatography (i.e. the peak shape, peak resolution, peak integration, retention times, and baseline) is acceptable.

The cursory review of chromatogram generated from instrument calibration and sample analyses shall include the following:

1. The signal from the FID or baseline is normal and the signal output is positive and on scale.
2. Chromatographic peaks are present, integrated correctly, and the peak shape is sharp.
3. The peak resolution or separation is acceptable based on historical instrument performance.
4. A flat or normal baseline at the end of the run usually is a good indicator that all components have been eluted from the analytical column.
5. No chromatographic abnormalities exist, such as large contamination or non-target co-eluting compounds, and electronic spikes.

Analytical instrument calibration is essential for the ultimate quality and usefulness of the data generated. Any software or calculation spreadsheet programs (Excel or Quattro Pro) implemented by the user must also be verified for accuracy.

Typically, a minimum of 10% of the data is processed through a secondary data review by the Quality Assurance Section. The secondary review involves checking the chromatogram, result reports, concentration, and peak identification results for consistency and accuracy.

H. Summary Report File or "Flat-File" Qualitative Comparison Review

VOCDat software is used to review daily results, and specific compounds such as propane and benzene are charted daily and tracked to monitor system performance over time. Diurnal graphs of hourly measurements at a site are very useful in clearly identifying trends and potential outliers. The Perkin Elmer system uses Totalchrom 6.2.2 software for data acquisition and processing.

Peak identification of the chromatographic peaks is done using retention time windows selected by the user. Several reference peaks are also selected to use relative retention times to correct for retention time shifting. Totalchrom 6.2.2 software has flexible post-run capabilities that allow the user to paste chromatograms or calibration plots into word processing software, graphically compare chromatograms, annotate chromatogram, and batch reprocess data.

I. Batch Reprocessing of Raw Data Files

The Perkin Elmer Ozone Precursor Monitoring System generates a total of 48 raw data files per day. Each night these files are automatically downloaded from the host computer at a particular site to a remote computer in the Air Toxic Monitoring laboratory at IDEM. These files are archived automatically on the data disk of the computer.

Changing environmental conditions alter the moisture content of the sample, resulting in shifting of retention times of analytes. Before batch reprocessing the data for a given day, it is necessary to update the retention times of the compounds in the calibration files.

J. Creating Sequence Files for Batch Reprocessing of Raw Data

All files necessary to generate a sequence file for batch reprocessing of raw data files are on the C: drive. Data processing methods are updated and renamed on each day which has a calibrant run in the sequence (every odd-numbered day of the month). Each day a new sequence is created in the Totalchrom Navigator as follows:

K. Examining the shift in retention times in a given RT window.

The maximum shift in retention time should occur during temperature programming of the GC. The shift is minimum during isothermal conditions. Beginning at minute 16, the temperature is increased at a rate of 5 °C/min for the next 25 minutes, and then raised to 200 °C at a rate of 15 °C/min in the next 3 minutes. It is prudent to examine 16-35 minute portions of the chromatogram. The entire chromatogram is examined in sections from beginning to end for shift in retention times of the peaks.

L. Data Quality Objectives:

Data quality objectives are defined by the overall quality requirements for the final use of the data. DQO's are expressed in terms of detection limit, accuracy, and precision.

1. In the absence of specified DQO's, the estimated detection limit for the target VOC's is 1 ppbC.
2. In the absence of specified DQO's, the absolute accuracy should be within 25% of the reference value.
3. The sampling manifold should be checked quarterly for leaks.
4. All canister samplers should be certified before and after ozone monitoring season.
5. Elapsed-time meter should be checked semi-annually.

6. The flow meter should be checked weekly.
7. The in-line particulate filter should be changed at least once per month.
8. All canisters should be cleaned, certified, and tagged for monitoring.

II. Audits:

There are three different types of audits used to determine whether criteria stipulated in the QA plan are being met:

1. **Technical System Audit:** This audit evaluates the entire measurement system. This includes the review of facilities, equipment, system, record keeping, data validation, operation, maintenance, calibration procedures, reporting requirements and QA procedures. The system audits are normally done immediately before, or shortly after system start-up. They should be repeated regularly, at least annually.
2. **Performance Evaluation Audit:** A performance evaluation audit involves the analysis of a reference material of known value. Performance evaluation audits should be conducted on a regular basis. For the PAMS program, the performance audits will be done every two weeks. The analysis results of the audits will be archived for comparison purposes.
3. **Data Quality Audits:** These audits include raw data recording and transfer, calculations and equations, documentation of data handling, reporting and completeness, and QA/QC requirements. A data quality audit for enhanced ozone monitoring should include an audit of the data entered into AQS.

APPENDIX H

Subject: Procedures for Carbonyl Monitoring and Handling DNPH Cartridges

Waters Sep-Pak DNPH-Silica cartridges consist of 2, 4 -diphenylhydrazine-coated silica packed in Waters Sep-pak plus cartridges equipped with end caps and plugs. The physical/chemical properties of the cartridges are as follows:

Hold-up volume	0.7 ml
Particle size	55 to 105 μm
Collection efficiency	>95% for sampling rates up to 2 l/min
Capacity	Approximately 75 μg formaldehyde
Quantity of DNPH Silica	0.35 g/cartridge (1.0 mg DNPH)
Operating temperature	10-100 $^{\circ}\text{C}$
Dimensions	4.3 cm total length 1.0 cm I.D. 0.9 cm bed length

During the PAMS monitoring season, eight samples are collected every three hours, every third day, starting June 1st through the end of August. Ambient air is passed through the ozone scrubber to remove ozone which degrades the hydrazone derivatives. The cartridges should be analyzed within two weeks of collection.

Procedure:

1. Take the cartridge from the pouch. Remove and save the end cap and plug.
2. Connect the cartridge to a sampler with flexible plastic tubing. The cartridge is bidirectional.
3. Record flow rate and collection time.
4. Reseal the cartridge with its end cap and plug. Store the cartridges in the user pouch with appropriate identification. If possible, seal the pouch using a heat sealer, or store the cartridges in a glass container with a Teflon lined cap. Keep samples refrigerated before and during shipping to contract laboratory for analysis.
5. Trip blanks: Every two weeks, one of the cartridges will be hooked up to the sequential sampler without flow. Then they are analyzed the same way as samples. Follow USEPA's monitoring schedule if provided.
6. Duplicates: A number of cartridges equal to 10% of the total number of samples should be run as duplicates. Hook up one of the cartridges to an empty port every other sampling day, and program it to run at the same time as one of the samples. Mark appropriately for sample analysis.

APPENDIX I

Procedure excerpt from SOP S-
022-OAQ-M-AM-12-T-R1

Subject: Toxic Sampler Setup and Pickup Lab Commerce – Meriter MCS-1-R

A. Canister Pick-up:

1. On sampler's front panel, record **ELAPSED TIME** (ET) in the onsite logbook. Reset ET using the red button on the meter.
2. Record final **CANISTER PRESSURE** in the onsite logbook. Final canister pressure should be approximately 5 to 7 psig.
3. Close canister valve & disconnect from sample line. Cap valve and remove canister.
4. Record final pressure, ET, and your initials on canister tag.

B. Sampler Flow Check & Water Trap Purge:

1. On timer, press **#1** button twice, press **#2** button twice: activates pump & solenoid valves.
2. Connect rotameter to canister sample line. Rotameter should read around 30 or the value which corresponds to 6.5 cc's (flow values are posted on the back of the rotameter).
3. Set sampler flow using the black **SET FLOW** knob located on the front panel.
4. Check and adjust (if necessary) sampler's back pressure to 20 psi using the **SET BACK PRESSURE** knob.
5. Front panel **WATER TRAP** port: remove cap. Block open port with finger, release, block port, release several times. Any moisture will "spit" out during release.
6. Replace cap on the **WATER TRAP** port.
7. Front panel timer, press **#1** twice, press **#2** twice to turn off the pump and valves.

C. Canister Installation:

Uncap valve on new canister and connect to sample line.

1. Open canister valve then close valve. Note value of the sampler's front panel **CANISTER PRESSURE** gauge. Pressure should be -29 to -30 psi. Wait 2 to 3 minutes to check for leaks. If there is no change in gauge value, proceed to step #4.

2. Drop in gauge value indicates leak. Reconnect lines and check areas of sampler for leaks. Repeat step #2.
3. Open canister valve (leave open).
4. Record vacuum, back pressure, initials, run date on canister's tag and in the on-site log book.

D. Program Purge & Run Date / Times:

Start Purge 30 minutes before midnight (day before sample date).

1. Press **Prog.** button.
2. Use **Select** and **Day** buttons to delete all days except the purge day (i.e. Tuesday).
3. Use the **h** button to set hour to 23.
4. Use the **m** button to set minutes to 30.
5. The display should read 2330.
6. Press **#1** & a circle with a black dot appears on display (channel is on).
7. Press **#2** & a broken/open circle \cap appears (channel is off).

Set Sample Start Time 1 minute after midnight.

1. Press **Prog.** button.
2. Use **Select** and **Day** buttons to delete all days except for sample day (i.e. Wednesday).
3. Use the **m** button to set minutes to 01. The display should read 0001.
4. Press **#1** and Press **#2** so that two black dot circles appear.

Set Sample Stop Time to 2359 minutes.

1. Press **Prog.** button.
2. Use the **Select** and **Day** buttons to delete all days except sample day (i.e. Wednesday).
3. Use the **h** button to set hour to 23 & use **m** button to set minutes to 59.
4. Press **#1** and Press **#2** to display two open/broken circles. $\cap \cap$
5. Press the clock button to activate channels 1 and 2.

- | | | |
|---------------------------------|------------|------------|
| | CH1 | CH2 |
| 6. The display should indicate: | \cap | \cap |

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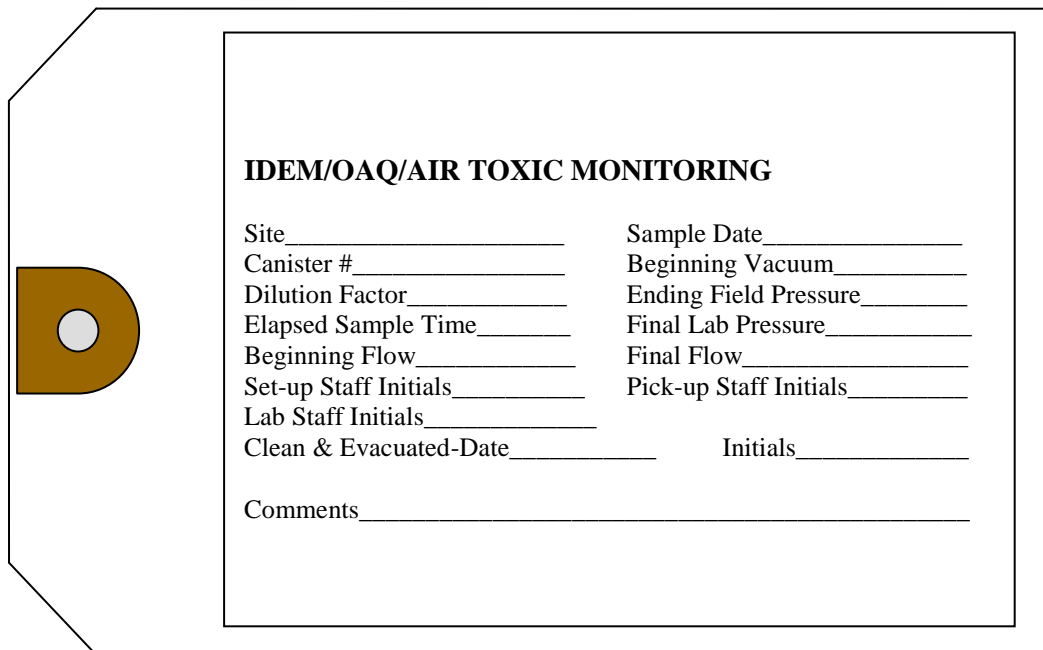
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Note: All applicable IDEM Toxics SOPs are found here:

https://extranet.idem.in.gov/main.php?section=standards&page=sops#oag_monitoring

ATTACHMENT #1

SUMMA Canister Chain-of-Custody Tag



The image shows a SUMMA Canister Chain-of-Custody Tag. It is a rectangular tag with a brown, semi-circular tab on the left side. The tag is divided into two main sections by a vertical line. The left section is for identification and the right section is for monitoring data. The right section is titled "IDEM/OAQ/AIR TOXIC MONITORING" and contains various fields for recording sample information.

IDEM/OAQ/AIR TOXIC MONITORING	
Site_____	Sample Date_____
Canister #_____	Beginning Vacuum_____
Dilution Factor_____	Ending Field Pressure_____
Elapsed Sample Time_____	Final Lab Pressure_____
Beginning Flow_____	Final Flow_____
Set-up Staff Initials_____	Pick-up Staff Initials_____
Lab Staff Initials_____	
Clean & Evacuated-Date_____	Initials_____
Comments_____	

ATTACHMENT #2

Monitored Compounds from Method TO-15 Compound List:

Propene	Dibromochloromethane
Freon-12	1,2-Dibromoethane
Chloromethane	Tetrachloroethene
Freon-114	Chlorobenzene
Vinyl chloride	Ethylbenzene
1,3-butadiene	m/p/o-Xylenes
Ethanol	Bromoform
Acetone	Styrene
Bromomethane	1,1,2,2-Tetrachloroethane
Chloroethane	1-Methylethylbenzene
Freon-11	para-Ethyltoluene
Isopropanol	1,3,5-Trimethylbenzene
Vinylidene chloride	1,2,4-Trimethylbenzene
Carbon disulfide	Benzyl chloride
Dichloromethane	1,3-Dichlorobenzene
Freon-113	1,4-Dichlorobenzene
trans-1,2-Dichloroethene	1,2-Dichlorobenzene
cis-1,2-Dichloroethene	1,2,4-Trichlorobenzene
Methyl tert-butyl ether	Hexachloro-1,3-butadiene
Methyl ethyl ketone	
Hexane	
Chloroform	
Ethyl acetate	
Tetrahydrofuran	
1,2-Dichloroethane	
1,1,1-Trichloroethane	
Benzene	
Tetrachloromethane	
Cyclohexane	
1,2-Dichloropropane	
Bromodichloromethane	
Trichloroethene	
1,4-Dioxane	
Heptane	
cis-1,3-Dichloropropene	
Methyl isobutyl ketone	
trans-1,3-Dichloropropene	
1,1,2-Trichloroethane	
2,3,4-Trimethylpentane	
Methylbenzene	
Methyl butyl ketone	

ATTACHMENT #3

Ozone Precursors:

Ethene	Styrene
Ethane	o-Zylene
Acetylene	Nonane
Propene	Isopropylbenzene
Propane	Propylvenzene
2-Methylpropane	m-Ethyltoluene
1-Butene	p-Ethyltoluene
Butane	o-Ethyltoluene
t-2-Butene	1,2,4-Trimethylbenzene
c-2-Butene	Decane
2-Methylbutane	1,2,3-Trimethylbenzene
1-Pentene	1,3,5-Trimethylbenzene
Pentane	m-Diethylbenzene
Isoprene	p-Diethylbenzene
t-2-Pentene	Undecane
c-2-Pentene	
2,2-Dimethylbutane	
Cyclopentane	
2,3-Dimethylbutane	
2-Methylpentane	
3-Methylpentane	
2-Methyl-1-pentene	
Hexane	
2-Methylhexane	
Benzene	
Cyclohexane	
2,3-Dimethylpentane	
3-Methylhexane	
Methylcyclopentane	
2,4-Dimethylpentane	
2,2,4-Trimethylpentane	
Heptane	
Methylcyclohexane	
2,3,4-Trimethylpentane	
Toluene	
2-Methylheptane	
3-Methylheptane	
Octane	
Ethylbenzene	
m+p-Xylene	

ATTACHMENT #4

Carbonyl Cartridge Chain-of-Custody Tag:

Site:_____

AQS:_____

Cartridge ID Number:_____

Run Date:_____

Time On:_____

Initial Flow:_____

l/min_____

Time Off:_____

Final Flow:_____

l/min_____

Single Run:_____

Duplicate Run:_____

Initial Leak Check:_____

Final Leak Check:_____